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THE STRUCTURE OF RYANODINE. I¹

By R. B. KELLY,² D. J. WHITTINGHAM,³ AND K. WIESNER

Abstract

Ryanodine consumes one mole of periodic acid and gives oxoryanodine $C_{25}H_{33}O_9N$. Splitting off water from ryanodine gives anhydroryanodine $C_{25}H_{33}O_8N$. The analyses of these two derivatives are therefore in agreement with the formula for ryanodine $C_{25}H_{35}O_9N$. Alkaline hydrolysis of ryanodine gives pyrrole- α -carboxylic acid and an alcohol $C_{20}H_{32}O_8$. This alcohol splits off water to give a compound $C_{20}H_{30}O_7$. Alkaline hydrolysis of oxoryanodine consumes three moles of alkali and gives a mixture of low molecular acidic products. Alkaline fusion of oxoryanodine gives a neutral aromatic nitrogen-free crystalline substance.

Folkers and associates (1) have isolated from the flacourtiaceous plant *Ryania speciosa* Vahl. the insecticidal principle ryanodine. They formulated it tentatively as $C_{25}H_{35}NO_9$ or $C_{26}H_{37}NO_9$. It melts at 219-220°C., is neutral to litmus, and shows six or seven active hydrogens. The ultraviolet absorption maximum is at 268.5 m μ .

We have repeated the isolation of ryanodine and the substance, purified by a nine-funnel countercurrent distribution between ether and water, analyzed reasonably well for $C_{25}H_{35}NO_9$. This formula is substantiated by two derivatives which are much more easily purified and analyzed.

Upon oxidation with periodic acid or lead tetraacetate, ryanodine consumes one mole of each reagent, respectively, and gives a compound which we call oxoryanodine $C_{25}H_{33}NO_9$, m.p. 227°C. No volatile carbonyl compound could be detected.

Oxoryanodine can be differentiated from ryanodine by its sparing solubility in alcohol, from which it can be obtained in high purity. Treatment of ryanodine with acids in ether, for instance sulphuric acid, gives a beautiful crystalline compound, anhydroryanodine $C_{25}H_{33}NO_8$, m.p. 275°C., which can be sublimed without decomposition for analysis.

Both oxoryanodine and anhydroryanodine have ultraviolet spectra identical with ryanodine. The infrared spectrum of ryanodine shows a single carbonyl peak at 1684 cm.⁻¹. Oxoryanodine, in addition to this, shows a second carbonyl

¹ Manuscript received May 3, 1951.

Contribution from the Chemistry Laboratories of the University of New Brunswick, Fredericton, N.B. Presented at the 3rd Summer Seminar in the Chemistry of Natural Products, July 10th-14th, Fredericton.

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peak at 1719 cm^{-1} . Anhydroryanodine shows in addition to the original carbonyl peak a second one at 1735 cm^{-1} . The splitting off of water is therefore connected with the appearance of a new carbonyl group.

However, the group splitting off water is different from the grouping which is oxidized by periodic acid since anhydroryanodine consumes, as does ryanodine, one mole of periodic acid or lead tetraacetate.

The ultraviolet spectrum of ryanodine is, as can be seen from Fig. 1, closely related to the spectrum of pyrrole- α -carboxylic ester. Also, the infrared spectra of both compounds show several parallel bands. Alkaline saponification of ryanodine results in the consumption of one mole of alkali and gives pyrrole- α -carboxylic acid, identified by the melting point of the ester and its ultraviolet spectrum.

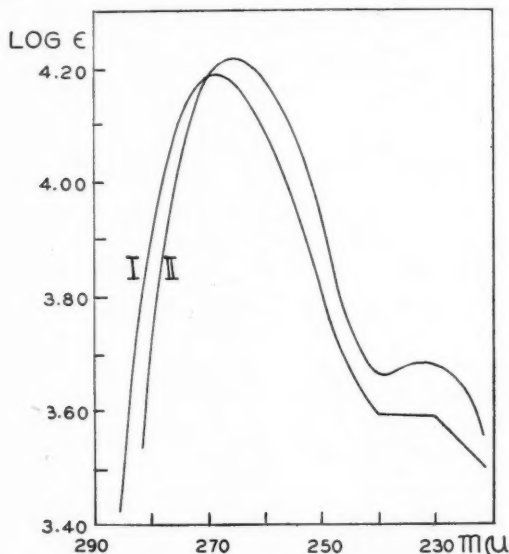


FIG. 1. Ultraviolet spectra in alcohols. I. Ryanodine. II. Pyrrole- α -carboxylic methyl ester.

Prolonged continuous extraction of the alkaline hydrolysis mixture gives a beautifully crystalline compound, m.p. $252^{\circ}\text{C}.$, which analyzes well for $\text{C}_{20}\text{H}_{32}\text{O}_8$. Active hydrogen determinations on this compound show a content of five or possibly six active hydrogens. A microhydrogenation failed to show the presence of double bonds. The compound has no ultraviolet absorption. The infrared spectrum of the compound suggests, in spite of the results of the microhydrogenation, the presence of double bonds, possibly of the $\text{R}_2-\text{C}=\text{CH}-\text{R}$ and $\text{RHC}=\text{CHR}$ type and besides this, of course, a strong peak due to bonded $-\text{OH}$ is observed. The compound does not show carbonyl absorption.

If the aqueous solution of the C_{20} alcohol is acidified, the compound can be extracted in a much shorter time on a continuous extractor. The compound thus obtained is difficult to crystallize but crystallizes on sublimation in high vacuum and melts then at 220°C . It analyzes for $C_{20}H_{30}O_7$. The infrared spectrum of this compound shows a carbonyl peak at 1720 cm^{-1} . Although this is not the exact value of the second carbonyl peak of anhydroryanodine, it seems reasonable to assume that the two compounds are in the same relationship as ryanodine and anhydroryanodine.

Alkaline saponification of oxoryanodine was also investigated. Somewhat surprisingly, the compound consumes three moles of alkali and gives a mixture of low molecular acidic products.

Alkali fusion of oxoryanodine gives besides pyrrole- α -carboxylic acid a neutral substance, m.p. 158°C . (in a low yield), which can be obtained in beautiful crystals and sublimed for analysis.

The ultraviolet (λ_{max} 258, $280\log\epsilon$ 4.00, 3.90) and infrared spectrum point to an aromatic compound.

The analysis checks best to $C_{12}H_{14}O_2$ although the formula $C_{18}H_{20}O_3$ has still to be considered.

Experimental Part

Ryanodine

The amyl acetate residue (6 gm.), prepared from 2400 gm. of *Ryania* powder according to the procedure of Folkers *et al.* (1), was dissolved in 300 ml. of ether and placed in a separatory funnel. Into a second and a third separatory funnel were placed 300 ml. of ether. After shaking the first funnel with 300 ml. of water, the water layer was transferred to the second funnel and a new 300 ml. portion of water was added to the first funnel. The process was repeated as in an ordinary countercurrent distribution until six portions of water had passed through the three funnels. The combined water layers were then evaporated *in vacuo* to a smaller volume and extracted six times with ether. The ether solution was evaporated to dryness, yielding 3-gm. of pure white foam. This material crystallized easily from ether, and after four recrystallizations attained a constant melting point of $228\text{--}229^{\circ}\text{C}$. It was dried at 80°C . for 24 hr. in high vacuum. Calc. for $C_{26}H_{36}NO_9$: C, 60.84; H, 7.15; N, 2.84%. Found: C, 60.44; H, 7.28; N, 2.88; active H, 1.36%.

Titration with lead tetraacetate or periodic acid gave a consumption of 0.83 mole of either reagent in 15 min. An extended reaction period did not alter this consumption.

Anhydroryanodine

Pure ryanodine (310 mgm.) was dissolved in 300 ml. of absolute ether and 0.5 ml. of concentrated sulphuric acid and 9 gm. of anhydrous copper sulphate were then added. The mixture was allowed to stand for three days. At the end

of this period the acid was neutralized by adding powdered sodium carbonate, and the ether solution was washed with a 5% sodium carbonate solution. The aqueous washings were extracted several times with ether, and the combined and dried ether extracts were taken to dryness. In this way 245 mgm. of a substance was obtained, which, after four crystallizations from methanol-chloroform, melted at 275°C.; further recrystallization did not alter the melting point. For analysis the compound was sublimed in high vacuum at 190°C. The melting point of the sublimate was 275°C. Calc. for $C_{25}H_{33}NO_8$: C, 63.14; H, 7.00; N, 2.95%. Found: C, 62.63, 62.65, 63.12; H, 6.96, 6.82, 7.17; N, 2.99, 2.89; active H, 1.26%.

Oxoryanodine

Ryanodine (250 mgm.) was dissolved in 5 ml. of methanol and to this solution was added 5 ml. of 0.5 *M* periodic acid and 2 ml. of water. After approximately ten minutes, oxoryanodine started to crystallize in shining rodlike crystals. In two hours the crystals were collected on a filter and washed with water. Upon drying the yield was 243 mgm. and the melting point 205-207°C. After six recrystallizations from methanol the compound melted constantly at 227°C. and gave a strong depression with ryanodine. For analysis it was dried at 110°C. for 24 hr. in high vacuum. Calc. for $C_{25}H_{33}NO_9$: C, 61.09; H, 6.77; N, 2.85%. Found: C, 61.26, 60.76, 60.69; H, 6.76, 6.64, 6.58; N, 3.21, 2.99, 3.33, 2.82; active H, 1.21%.

A nine-funnel countercurrent distribution of oxoryanodine between ether and water (200 ml. of each phase) gave the following result:

Funnel No.	Weight of substance
1	868 mgm.
2	67
3	1
4, 5, 6, 7, 8, 9	0

Alkali Fusion

Oxoryanodine (4.5 gm.) was added in small portions with stirring to 30 gm. of fused potassium hydroxide at 320-330°C. in a nickel crucible. After cooling, the melt was dissolved in 250 ml. of water and ice, and the solution was continuously extracted with ether for 24 hr. The ether extract was dried over anhydrous sodium sulphate, the greater portion of the ether was removed by distillation through a 12-in. Vigreux column, and the final traces of solvent were removed *in vacuo* at 10°C. The residue (167 mgm.) was dissolved in ether and this solution was chromatographed in ether on alumina. The residue from the eluate (98 mgm.) was sublimed at 40-60°C./0.15 mm. Part of the oily sublimate crystallized from petroleum ether in red-coated warts. This material (20 mgm.) was recrystallized twice and sublimed at 110°C./0.015 mm. to give white needles which melted at 158°C. Calc. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%; calc. for $C_{13}H_{20}O_3$: C, 76.03; H, 7.09%. Found: C, 75.35; H, 7.18%.

The aqueous solution, which had been continuously extracted with ether, was acidified to Congo red with sulphuric acid and then extracted continuously with ether for 24 hr. After removal of the ether, 2.5 gm. of a dark resinous material was obtained. This material was sublimed at 80°C./0.15 mm. to give a white solid. Three recrystallizations from ether - petroleum ether and re-sublimation at 95°C./0.015 mm. gave a pure substance which sublimed at 175-180°C. when subjected to a melting point determination. A positive test was obtained with alcoholic ferric chloride solution. Calc. for $C_6H_5NO_2$: C, 54.05; H, 4.53; N, 12.61%. Found: C, 54.15, 54.31; H, 4.40, 4.28; N, 12.54, 12.72%. The ultraviolet spectrum in alkaline alcohol showed λ_{\max} 253 m μ ; log ϵ 4.14 and in acidic alcohol showed λ_{\max} 264 m μ ; log ϵ 4.23.

The acidic substance (124 mgm.) was converted to the methyl ester with methanol and an ethereal solution of diazomethane. The product was recrystallized once from ether - petroleum ether, and then sublimed at 50°C./0.015 mm. to give beautifully crystalline rods, m.p. 73-74°C. alone and in admixture with an authentic specimen of the methyl ester of α -pyrrole carboxylic acid. Calc. for $C_6H_7NO_2$: C, 57.60; H, 5.64; N, 11.19%. Found: C, 57.59, 57.33; H, 5.31, 5.20; N, 10.87, 10.71%.

Saponification of Ryanodine

Ryanodine (2.7 gm.) was refluxed with 50 ml. of 5% alcoholic potassium hydroxide for six hours. After evaporation of the alcohol *in vacuo*, 50 ml. of water was added and the solution extracted continuously with ether for a week. Evaporation of the ether gave a white foam which crystallized in beautiful prisms from ether. The yield was 1.4 gm. After six crystallizations the m.p. was sharp and constant at 252°C. It was dried for analysis at 80°C. in high vacuum. Calc. for $C_{20}H_{32}O_8$: C, 59.97; H, 8.07%. Found: C, 59.97, 59.90; H, 7.95, 7.99%; active H, 1.27%; N, 0.00%.

Microhydrogenation: no uptake in glacial acetic acid with Adams catalyst.

From the exhausted residue pyrrole- α -carboxylic was extracted after acidification and identified by spectrum and mixed melting point of the methyl ester.

In another experiment performed analogously the hydrolysis mixture was immediately acidified, and extracted six times with ether which removed the pyrrole- α -carboxylic acid.

After this an 18-hr. continuous extraction gave a quantitative yield of a white foam which could only be precipitated as a powder by petroleum ether from ether and after a few reprecipitations crystallized on sublimation (m.p. 220°C.) Calc. for $C_{20}H_{30}O_7$: C, 62.80; H, 7.92%. Found: C, 62.53; H, 7.87%; N, 0.00%.

The analyses were performed in the microanalytical laboratory of Dr. R. Dietrich, Zurich.

Acknowledgments

The infrared spectra were taken partly in the National Research Council Laboratories, Ottawa, through the courtesy of Dr. R. Norman Jones and partly by Dr. Bohon in the Anderson Physical Laboratory; to them we are also indebted for their interpretation. The work was performed on a grant from the National Research Council, Ottawa.

We also wish to thank S. B. Penick and Company for a gift of powdered *Ryania* stems.

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STUDIES IN THE POLYOXYPHENOL SERIES

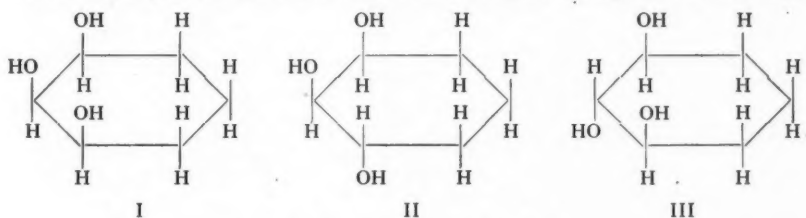
V. PREPARATION FROM PYROGALLOL OF THE ISOMERIC CYCLOHEXANE-1,2,3-TRIOLS AND -1,2-DIOLS, AND OF SEVERAL ISOPROPYLIDENE AND MONOMETHYL DERIVATIVES¹BY W. R. CHRISTIAN,² C. J. GOGK,³ AND C. B. PURVES

Abstract

A study of the high pressure hydrogenation of pyrogallol over nickel, copper - chromium oxide, and palladium catalysts showed that yields of 35% to about 60% of *cis-cis-cis*-cyclohexane-1,2,3-triol were attainable, but that the *cis-cis-trans* and *cis-trans-cis* isomers were formed only in minor amount. Partial hydrogenolysis of these primary products incidentally yielded some *cis*-cyclohexane-1,2-diol, a smaller amount of the *trans* form, but none of the 1,3-diols. The following derivatives were prepared apparently for the first time: *cis-cis*-isopropylidene-*cis*-cyclohexane-1,2,3-triol, an oil, and its monobenzoate, m.p. 103°C.; *cis-cis*-isopropylidene-*trans*-cyclohexane-1,2,3-triol, m.p. 51°C., and its monobenzoate, m.p. 72° to 76°C.; *cis*-monomethyl-*cis-cis*-cyclohexanetriol, m.p. 71°C., and its *bis*-3,5-dinitrobenzoate, m.p. 190°C.; *trans*-monomethyl-*cis-cis*-cyclohexane-1,2,3-triol, m.p. 37°C.; and isopropylidene-*trans*-cyclohexane-1,2-diol, an oil. Formation of the latter compound occurred when *p*-toluene-sulphonic acid, and not the customary hydrogen chloride, was used as catalyst in the condensation of the *trans* diol with acetone.

Introduction

The high pressure hydrogenation of pyrogallol led Lindemann and de Lange (15) to the three isomeric cyclohexane-1,2,3-triols (Structures I, II, III) which were separated and characterized in a satisfactory way for the first time.



The three cyclohexane-1,2,3-triols

These authors realized that the *cis-cis-trans* isomer could be identified because it was the only one capable of being resolved into D and L forms, but their failure to establish this fact decisively made their allocations of structure doubtful. In 1944 McRae and Moir (17) reviewed the literature and arrived

¹ Manuscript received June 7, 1951.

Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from Ph.D. Theses submitted in September 1946 (W.R.C.) and in April 1947 (C.J.G.).

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³ Present address: Corn Products Refining Company, Argo, Ill.

at the correct allocations by applying modern theory to the published data. This review will be given in a forthcoming article. In 1947 Posternak and Ravenna (23) published the first direct experimental proof of the configurations and their work included a resolution of the *cis-cis-trans* raceme by microbiological methods. The object of the present work was to determine the yields, unreported by Lindemann and de Lange, of cyclohexanediols and -triols obtainable by hydrogenating pyrogallol, and to study the possibility of separating the triols by the selective formation of their cyclic isopropylidene acetals. Posternak and Ravenna sought in vain to prepare such derivatives. Their data on the relative rates with which lead tetraacetate and the periodate ion oxidized the three triols were also supplemented by larger-scale experiments, since these rates differentiated the *cis-cis-cis* from the *cis-trans-cis* form.

A series of comparable high pressure hydrogenations of pure pyrogallol in ethanol were carried out at $100^\circ \pm 3^\circ\text{C}$. over Raney nickel instead of over the nickel-copper-cobalt catalyst used by Lindemann and de Lange (15). After various times aliquots of the filtered solutions were used to estimate unreacted pyrogallol. Destruction of the latter in the remainder of the products by air and alkali then left black liquors from which fractional distillation at 0.15 mm. pressure recovered the cyclohexanediols (b.p. 85° to 90°C .) and -triols (b.p. 119° to 123°C .). The yields were corrected for distillation losses but could not be regarded as precise. Fig. 1 (filled circles) shows that the maximum yield of cyclohexanetriols (42%) occurred after about 1.6 hr., or when about 70% of the pyrogallol had reacted. The formation of cyclohexanediols passed through a clearly marked induction period (open circles)

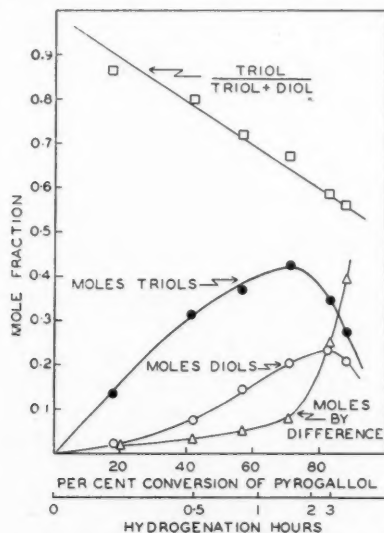


FIG. 1. High pressure hydrogenation of pyrogallol over Raney nickel at $100 \pm 3^\circ\text{C}$. to cyclohexane-1,2,3-triols and -1,2-diols.

and the molar ratio of triols alone to diols *plus* triols, when plotted against the percentage of pyrogallol reacted, gave a nearly linear relationship (squares). A somewhat questionable extrapolation of this ratio suggested that its value was unity at zero time, or that diols were not then present. These observations made it extremely likely that pyrogallol was first reduced to the cyclohexanetriols, and that the latter then underwent hydrogenolysis of hydroxyl groups to yield the diols. More volatile fractions, not recovered quantitatively, contained cyclohexanol (triangles). The difficulty of hydrogenolysis was encountered in an acute form by Packendorff (22), whose platinum oxide catalyst gave cyclohexane and cyclohexanol as the main products from catechol, resorcinol, and pyrogallol.

In larger-scale preparations at 130° to 140°C. in a bigger autoclave, it was found convenient to isolate the crude cyclohexanetriols by first evaporating the alcohol from the filtered hydrogenated liquor, and then extracting products of hydrogenolysis and unchanged pyrogallol with ether from an aqueous solution of the residue. As Lindemann and de Lange (15) reported, dilution of the re-distilled product with acetone separated much of the *cis-cis-cis*-cyclohexanetriol in crystalline form, and the pure *cis-cis-trans* and *cis-trans-cis* isomers could be isolated as crystalline tribenzoates from the mother liquors. Trial showed that these separations were not clean-cut and mother liquors had to be re-worked by benzylation and debenzoylation in a very tedious manner. The final yields (Table I) were nevertheless sufficiently accurate

TABLE I
YIELDS OF THE CYCLOHEXANE-1,2,3-TRIOLS FROM HYDROGENATED PYROGALLOL*

Catalyst, 100–145°C.	<i>cis-cis-cis</i> M.p. 108°C. %	As tribenzoates	
		<i>cis-cis-trans</i> M.p. 184°C. %	<i>cis-trans-cis</i> M.p. 142°C. %
Raney Ni**	12–24	0.3–6	0–1.1
Ni – Supercel***	6.3	0.8	0.7
Cu – Cr – O†	17	6.8	3.2
Pd – SrCO ₃ ††	70–77	~5†††	0†††

* Hydrogenated at 2400 to 3100 p.s.i. initial pressure until residual pyrogallol was 10 to 30%.

** Five runs using 25 to 316 gm. of pyrogallol at 100° to 140°C.

*** Used at 140°C.

† Experiment at 140° to 145°C. by C. Gleason.

†† Experiment in pure 1,4-dioxane at 130° to 135°C. by J. F. C. Dixon.

††† Larger-scale separations by N. S. Whittall.

to confirm the fact that the hydrogenation of pyrogallol with nickel catalysts was a practical preparative method for *cis-cis-cis*-cyclohexanetriol. Such catalysts, however, were of doubtful utility for the other two isomers, which were recovered in improved, but still unsatisfactory, yields by hydrogenating over copper – chromium oxide. A new palladium–strontium carbonate catalyst (19) promoted comparatively little hydrogenolysis but the crude cyclo-

hexanetriols consisted overwhelmingly of the *cis-cis-cis* isomer and none of the *cis-trans-cis* isomer was isolated from special larger scale experiments carried out recently in this laboratory by Mr. N. S. Whittall.

The preponderance of the *cis-cis-cis* form in all the hydrogenations studied could be accounted for by the "normal" or "one-sided" addition of hydrogen to pyrogallol molecules adsorbed plane to the flat surface of a crystalline catalyst (12). The occurrence of the *trans* forms, however, would seem to require either a multi-stage hydrogenation of the aromatic ring, or a keto-stage, or a thermal isomerization. Although such a thermal isomerization actually took place when *cis*-1,2-dimethyl cyclohexane was passed over nickel at 170°C. (18, 27), a keto-stage mechanism seemed more probable in the present case because Coussemant and Jungers (6) isolated up to 18% of cyclohexanone as an intermediate in the high pressure hydrogenation of phenol. The recovery of *cis-cis-cis*-cyclohexanetriol exclusively from the hydrogenation of optically active *cis*-2,3-dihydroxycyclohexanone over platinum oxide (23), however, raised an objection to this analogy.

On one occasion the entire cyclohexanediol fraction was found to reduce the amount of periodate calculated for the exclusive presence of 1,2-diols (see below). Cyclohexane-1,3-diols, which would be stable to periodate, were therefore present, if at all, in extremely small amount, as was expected from the known tendency for hydrogenolysis to eliminate hydroxy groups in a β , rather than an α , position to others (1, p. 69). The predominance of *cis*-1,2-diol over the *trans* form (mole ratio 2:1) reflected the much greater amount of *cis-cis* triol initially produced by the hydrogenation.

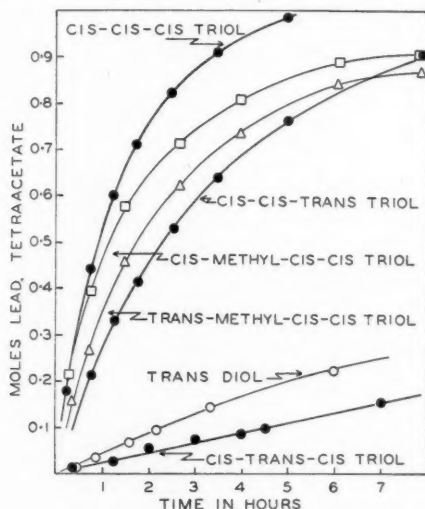


FIG. 2. Rates of oxidation, in glacial acetic acid at 18.6°C., of 0.0025 M solutions of the cyclohexane-1,2,3-triols and -1,2-diols; triols with 0.00665 M, and diols with 0.005 M, lead tetraacetate. Plot for the *cis* diol (not shown) was superposable on that for the *cis-cis-cis* triol. Similar oxidations of the monomethyl ethers at 20°C.

Criegee's (7) oxidations of the cyclohexanediols with lead tetraacetate at 18°C. proceeded with second order rate constants of $10^3 K = 80$ and 25 (liters/mole/sec.), respectively, for the *cis* and *trans* forms. A repetition of this work (Fig. 2 and Table II) gave a divergent result for the *cis* diol, but such rates were shown to be sensitive to small amounts of water in the lead

TABLE II
SECOND ORDER RATE CONSTANTS FOR OXIDATIONS WITH
LEAD TETRAACETATE AND THE PERIODATE ION

Substance	Pb(OAc) ₄		KIO ₄ *** 10 ³ K**
	C × 10 ³ *	10 ³ K**	
Cyclohexanediols			
<i>cis</i>	4.98	54 80†	1.5
<i>trans</i>	5.00	27 25†	0.22
Cyclohexanetriols			
<i>cis-cis-cis</i>	3.30 6.63 13.1	36 36 30	120
<i>cis-cis-trans</i>	3.30 6.63 13.1	14 14 12	0.59
<i>cis-trans-cis</i>	6.69	1.0	0.12
3-Methoxycyclohexane-1,2-diols††			
<i>cis-cis-cis</i>	5.7	21	
<i>cis-cis-trans</i>	5.7	48-26	

* Concentration C in mole per liter at 18.6°C. Glycol 0.003 M in all cases.

** Second order rate constant K in liter/mole/sec.

*** A 0.004 M solution at pH 11.6 and 20.0°C.; glycol concentration 0.0025 M.

† Criegee's results as 18.0°C. (Ref. 7).

†† At 20°C. for 0.0024 M glycol solutions.

tetraacetate-acetic acid solution (8). The *cis* form was also oxidized much more rapidly than the *trans* form by aqueous sodium periodate at pH 11.6, as Price and Knell (24) had previously shown, although the figure they used to publish their data did not lend itself to a quantitative comparison with the present results (Fig. 3 and Table II). The oxidations of the cyclohexane-1,2,3-triols were carried out with the same experimental conditions and the *cis-cis-cis*, *cis-cis-trans*, and *cis-trans-cis* isomers reacted at diminishing rates, both with lead tetraacetate and sodium periodate, as expected from the work of Posternak and Ravenna (23). Although each mole of triol should in theory consume two moles of either oxidant and liberate one mole of formic acid, the utilization of the second mole was slow and the oxidations in their later stages failed to follow the second order rate constants noted in Table II. It is apparent from Fig. 3 that traces of the *cis-cis-cis* and *cis-cis-trans* forms could be removed from the *cis-trans-cis* triol by a selective oxidation with periodate, although no use was made of this observation in the present research.

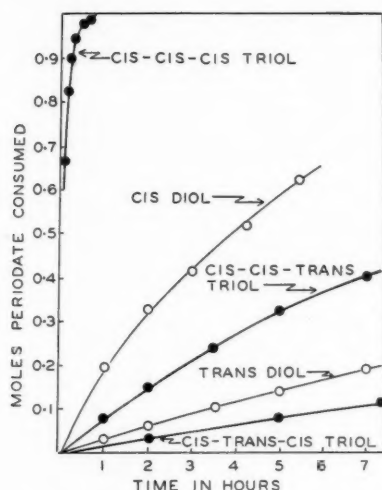
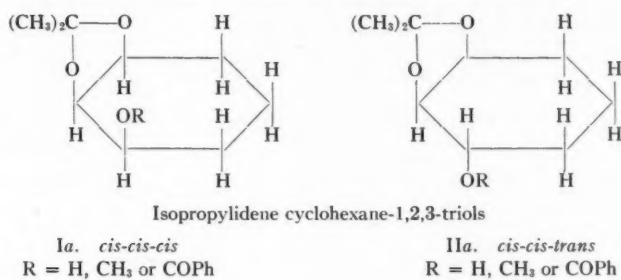


FIG. 3. Rates of oxidation, by 0.004 M aqueous periodate at pH 11.6 and 20°C., of 0.003 M solutions of the cyclohexane-1,2,3-triols and -1,2-diols.

By condensing glycols, usually in presence of hydrogen chloride as a catalyst and anhydrous sodium sulphate as a dehydrating agent (Method B) Böeseken (3) established the generalization that cyclic isopropylidene derivatives would form only with 1,2-diols in which the contiguous hydroxy groups were in favorable proximity and in the same plane as the carbon atoms to which they were attached. This rule explained the existence of isopropylidene derivatives from *cis*-1,2-cyclopentanediol and *cis*-1,2-cyclohexanediol, but not from the corresponding *trans* isomers. The cyclohexanediols were separated very efficiently on several occasions (2, 9, 26) by taking advantage of this circumstance. An attempt was made to apply the same principle of separation to a mixture of the cyclohexanetriols, but the condensation with acetone happened to be carried out with *p*-toluenesulphonic acid as catalyst and a continuous azeotropic distillation with ligroin as the means of dehydration (21) (Method A). Acid hydrolysis of the mixed isopropylidene derivatives, however, yielded a little *cis-trans-cis*-cyclohexanetriol and it was plain that this all-*trans* isomer had unexpectedly undergone the condensation. It then transpired that Method A readily produced a 67% yield of the hitherto unknown isopropylidene acetal from *trans*-cyclohexane-1,2-diol as an oil with a strong peppermint odor, whereas Method B yielded not more than 3%. The attempts of Maan (16) to obtain isopropylidene acetals from several substituted *trans*-cyclohexane-1,2-diols resulted in traces of volatile oils which were assumed, probably in error, to be condensation products of acetone itself. *cis-cis-cis*-Cyclohexanetriol, however, gave with both methods nonquantitative yields of uncrystallized, very readily hydrolyzed acetals (Ia, R = H) which were separately methylated with silver oxide and methyl iodide. Since some



hydrolysis of the labile acetal bonds probably occurred during this process, the crude monomethyl derivatives (Ia, R = CH₃) were straightway hydrolyzed with dilute acid, and yielded one and the same crystalline monomethyl cyclohexanetriol. The behavior of the *cis-cis-trans*-cyclohexanetriol was similar, although in this case the isopropylidene derivative (IIa, R = H) was crystalline and the crystalline monomethyl ether of the triol was distinguished by its great hygroscopicity. Both of the cyclohexanetriols yielded crystalline isopropylidene monobenzoates. The ready oxidation of the *cis-cis-cis* monoether with lead tetraacetate (Fig. 2) proved that it still contained an unsubstituted 1,2-glycol group and confirmed the structure (Ia, R = CH₃) assigned to its isopropylidene derivative. Moreover, since the glycol unit in this case was obviously *cis*, and since the oxidation proceeded almost as quickly with the monomethyl ether of *cis-cis-trans*-cyclohexanetriol (Table II, Fig. 2) the latter also retained the unsubstituted *cis*-1,2-glycol unit. This argument checked the validity of the structures (IIa).

It was, of course, recognized many years ago that an occasional *trans*-1,2-glycol, such as that from cycloheptane (4, 9), yielded an isopropylidene derivative when condensed with acetone according to the general method A. The present work shows that with *trans*-cyclohexanediol Method B succeeded and Method A failed, and that in consequence Böeseken's generalizations about the formation of isopropylidene derivatives may not apply with the same force when the method of condensation is radically changed.

Experimental

Hydrogenation of Pyrogallol

With Raney Nickel Catalyst (20)

(a). The data summarized in Fig. 1 were based on uniform hydrogenations each employing 25.2 gm. of resublimed pyrogallol, 150 cc. of absolute ethanol and 5.0 gm. (wet with ethanol) of catalyst. A Parr high pressure hydrogenation apparatus with a 500 cc. stainless steel bomb was used. After flushing out the system several times with hydrogen, the pressure was adjusted to 2400 p.s.i., the bomb was rapidly heated to 100°C. and maintained within $\pm 3^\circ\text{C}$. of that temperature. As the temperature reached 100°C. the shaking device was set in motion and hydrogenation was assumed to have begun at

that moment. After four hours or less, the bomb was rapidly quenched in cold water, the contents were filtered to remove the catalyst, and filtrate and washings were made up to 280 cc. with ethanol.

Gardner and Hodgson's method (11) was used to determine the unreduced pyrogallol in 0.1 cc. aliquots of the above solution. Each aliquot was added to 25 cc. of 0.1 *N* iodine - potassium iodide solution and strong caustic soda was then added drop by drop until the mixture just failed to give a blue color with a starch indicator. Thirty minutes later 100 cc. of water and 5 cc. of concentrated hydrochloric acid were added, and the liberated iodine was titrated with 0.1 *N* sodium thiosulphate. If the reagent blank was x cc., the titer of the original pyrogallol solution, y cc., and that of the solution after the hydrogenation, z cc., then the residual pyrogallol was $100(x-z)/(x-y)\%$ of the original amount. Control experiments showed that the estimation was reliable to $\pm 5\%$ even in the presence of ethanol, cyclohexanediols and triols, and the substances arising from the alkaline oxidation of pyrogallol (see below). The amount of iodine required by one mole of pyrogallol, however, was almost 5 moles; not 3 moles, as stated by Gardner and Hodgson, or 3.85 moles as calculated from the example they gave.

The remainder of the hydrogenation liquor was diluted with three 50 cc. volumes of strong aqueous ammonia, added over a period of five hours while oxygen gas was bubbled through the mixture to destroy any pyrogallol. Evaporation of solvents from the resulting black liquor, followed by fractional distillation at 15 mm. pressure, yielded the cyclohexanediol fraction, b.p. 85° to 90°C . and the triol fraction, b.p. 119° to 123°C . Both fractions gave a negative ferric chloride test for phenols. Trials with known mixtures showed that the loss of cyclohexanediols in the fractionation was about 2%, and that of the triols about 6%. The data in Fig. 1 were corrected accordingly.

(b). Hydrogenations on a larger scale (Table I) were carried out in a 2-liter Aminco stainless steel bomb and with a more convenient method of isolation. In a typical run, 316 gm. (2.5 moles) of pyrogallol dissolved in 1000 cc. of ethanol were hydrogenated over 50 gm. (wet) of Raney nickel for three hours at 140°C . and 3000 p.s.i. of hydrogen. The hydrogen absorbed was 8.5 moles, instead of the 7.5 moles required for a quantitative conversion to cyclohexane triols. After removal of the catalyst and the ethanol, distillation of the residue yielded 290 gm. of a clear, partly crystalline fraction boiling at 90° to 135°C . at 0.05 mm. pressure. A solution, 500 cc., of this product in water was then extracted continuously with ether to remove cyclohexanediols and also 30 gm. (10%) of unreduced pyrogallol. Evaporation and fractional distillation of the aqueous residue then yielded 90.7 gm. (33%) of cyclohexane-triols boiling at 120° to 140°C . at 0.02 mm. pressure.

With Copper - Chromium Oxide Catalyst (5)

The catalyst, 20 gm., was added to 63 gm. (0.05 mole) of pure pyrogallol dissolved in 200 cc. of pure 1,4-dioxane and hydrogenation was with 3100 p.s.i. of hydrogen at 140° to 145°C . for 150 min. Hydrogen absorbed was 1.68 moles,

or about 10% in excess of theory. The crude cyclohexanetriols, isolated as in (b) and weighing 20.2 gm. (30.6%) were separated as described below into the three isomers, all with correct melting and mixed melting points (Table I).

With a Palladium - Strontium Carbonate Catalyst

As the originators noted (19), this catalyst was very readily inactivated by adventitious impurities, which had to be rigorously eliminated from the reagents. Inactivation uniformly occurred in a 2-liter Aminco stainless steel bomb but not in one of 500 cc. capacity, even when the rates of heating were equalized and the same solutions and catalyst were used. The catalyst, 12 gm. containing 2% of palladium, 33.3 gm. of pyrogallol, 200 cc. of dioxane, and hydrogen initially at 2400 p.s.i. were kept at 75° to 80°C., little or no hydrogen being absorbed at a lower temperature. After two hours of hydrogenation the theoretical amount had been absorbed and the reaction apparently ceased. Much of the *cis-cis-cis*-cyclohexanetriol formed was found to have crystallized and concentration of the mother liquor raised the recovery to 17.6 gm. (50%). The residues when worked up as in (b) yielded a further 27% of the mixed *cis-cis-cis* and the *cis-cis-trans* isomers. In larger scale experiments the residual mixture was benzoylated, but extensive fractional crystallization of the tribenzoates revealed no trace of the *cis-trans-cis* form.

Separation of the Cyclohexanetriols

The method of Lindemann and de Lange (15) was followed in principle. A crude cyclohexanetriol fraction, 84 gm., b.p. 135° to 140°C. at 0.25 mm. pressure, was heated under reflux with 1400 cc. of acetone for 10 min. and the mixture was then kept at -15°C. Next day the undissolved portion (45.5 gm.) on recrystallization from an acetone-ethanol mixture yielded 31.7 gm. of the *cis-cis-cis* isomer with the correct melting point of 147° to 147.5°C. In other runs the recrystallizations were more advantageously carried out from ethyl acetate-acetone mixtures. Small amounts of the other two isomers were recovered as the tribenzoates from the final mother liquors.

The acetone-soluble portion, about 40 gm., after recovery was heated on the steam bath for one hour with benzoyl chloride, 110 cc., and pyridine 100 cc. Solution of the semisolid benzoates in 750 cc. of hot ethanol, followed by cooling overnight to room temperature, caused the deposition of the crude crystalline *cis-cis-trans* tribenzoate, which was extracted with 250 cc. of hot ethanol. The tribenzoate, 35.8 gm., was then nearly pure and was conveniently recrystallized to the proper melting point of 182°C. (uncorr.) from glacial acetic acid. The alcohol mother liquors from the crude tribenzoate were kept overnight at -15°C. to bring about the crystallization of the crude *cis-trans-cis* isomer (12.1 gm.). Two recrystallizations from methanol, preferably containing about 5% of water, yielded 5.4 gm. of this isomer with the correct melting point of 139° to 140°C. Mother liquors from all the above crystallizations were then combined, de-benzoylated, and recycled to yield a further 15.1 gm. of *cis-cis-cis*-cyclohexanetriol, 14.1 gm. of the *cis-cis-trans*-

tribenzoate, and 0.8 gm. of the *cis-trans-cis*-tribenzoate. The final residues from another run were shown to contain a trace of *trans*-cyclohexanediol, which was isolated as the isopropylidene derivative.

The hydrolyses of the two tribenzoates with five volumes of 10% methanolic potassium hydroxide at 45°C. was allowed to continue for several hours after solution was complete, and the products were isolated as Lindemann and de Lange described. A yield of 78% of *cis-cis-trans*-cyclohexanetriol, with the correct melting point of 124°C. was obtained after recrystallization from ethyl acetate. The *cis-trans-cis* isomer (73% yield) melted at 110° to 110.5°C. after recrystallization from ethyl acetate, whereas the recorded m.p. was 108°C. Unlike the other two isomers, the *cis-trans-cis* form was noticeably hygroscopic.

Separation of cis and trans Cyclohexanediols

The crude diol fraction, melting at 76° to 85°C., when triturated with benzene left a residue of the crude *cis* isomer, which could be recrystallized to the proper m.p. of 99°C. from a hot solution of the same liquid. After recovery from the benzene mother liquors, the residue on recrystallization from a 1:2.5 acetone-ligroin mixture deposited the crude *trans* diol, which attained the correct m.p. of 103° to 104°C. when recrystallized from ethyl acetate. The identity of the *cis* and *trans* cyclohexanediols was confirmed by mixed melting points with authentic specimens obtained by oxidizing cyclohexene with potassium permanganate (16) and hydrogen peroxide (26) respectively.

A much more satisfactory method was to separate the *cis* as its more volatile isopropylidene derivative from the *trans* diol, according to the procedure of Rothstein (25). A 46.9 gm. sample of the mixed diols from a large-scale hydrogenation of pyrogallol yielded 39.9 gm. of isopropylidene *cis*-1,2-cyclohexanediol boiling at 70° to 71°C. (12 mm.), together with a still residue from which 13.8 gm. of pure *trans* diol was recovered by crystallization from hot benzene. Hydrolysis of the isopropylidene derivative by heating for two hours with 100 cc. of acetone and 10 cc. of concentrated hydrochloric acid gave 28.5 gm. of the *cis* diol, which was recrystallized from an acetone-petroleum ether mixture cooled to -15°C.

Condensations with Acetone

Method A

A 5 gm. to 7 gm. sample of the pure diol or triol was heated under reflux with about 0.1 gm. of *p*-toluenesulphonic acid monohydrate, 150 cc. of purified acetone and 150 cc. of petroleum ether (b.p. 30° to 60°C.). The apparatus, similar to that of Newman and Renoll (21), consisted of a 500 cc. round-bottomed flask attached by a glass joint to a condenser half-filled with water. This condenser returned acetone vapor to the flask but permitted the water formed in the reaction to pass (as an azeotrope with petroleum ether) into a

second, more efficiently cooled condenser and to be removed by a trap from the system. The condensation was judged to be complete when water ceased to accumulate in the trap. A small amount of anhydrous sodium acetate was added to the residual liquors to neutralize the sulphonic acid before they were evaporated under reduced pressure.

Method B

Five gm. of the diol or triol and 3 gm. of anhydrous sodium sulphate were mechanically shaken with 300 cc. of pure acetone containing 1% or less of dry hydrogen chloride (3), usually for 24 hr. The acid was neutralized with basic lead carbonate; the filtrate from this operation was made definitely alkaline with dry ammonia gas and was evaporated *in vacuo*.

cis-cis-Isopropylidene-*cis*-Cyclohexanetriol

Method A after two days of heating under reflux gave a still residue which was extracted with benzene. Fractional distillation of the extract returned a 92% yield of the product as a clear colorless oil boiling at 113° to 115°C. (18 mm. pressure). Method B using 1% hydrogen chloride gave a 69% yield (b.p. 111° to 114°C. at 16 mm.), but toward the end of the fractionation white crystals, presumably of regenerated triol, appeared in the neck of the distillation flask. The product from both preparations was soluble in common organic liquids but was practically insoluble in water. All attempts to crystallize the oil failed. Its instability was such that a sample kept for two weeks in a tightly stoppered flask had hydrolyzed completely to the cyclohexanetriol with the correct m.p. of 148°C. after recrystallization. Incipient decomposition was probably the cause of difficulties encountered in the combustion of the isopropylidene derivatives, the best of several results being C, 62.4; H, 8.9%. Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4%.

cis-cis-Isopropylidene-*trans*-Cyclohexanetriol

After 60 hr. of heating under reflux, the product from Method A was an oil boiling at 128° to 131°C. at 19 mm. pressure. The oil crystallized completely and recrystallization from ligroin left a 53% yield of fine white needles melting at 50° to 51°C., not depressed by admixture with the product from Method B (0.2% hydrogen chloride). This specimen was initially isolated in 70% yield but two recrystallizations from ligroin at less than 0°C. reduced the amount of pure material, m.p. 51°C., to 45%. Found: C, 63.0; H, 9.5%. Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4%.

The compound had the solubilities of the *cis* isomer but was much more stable, a sample stored in a tightly stoppered tube deteriorating only very slightly during several weeks.

Isopropylidene-trans-Cyclohexanediol

Method A and 60 hr. of heating yielded 67% of a colorless oil boiling at 77° to 78°C. at 20 mm. pressure, with a density, d_4^{20} , 0.9787 and a refractive index, n_D^{20} 1.4468. Found: C, 69.6; H, 10.3%; mol. refraction, 42.65. Calcd.

for $C_9H_{16}O_2$: C, 69.2; H, 10.3%; mol. refraction, 42.66. Unreacted *trans*-cyclohexanediol was recovered in 9% yield from a benzene extract of the still residue.

The isopropylidene derivative could not be induced to crystallize, had a strong peppermint odor, and was freely soluble in common organic liquids. A 1-gm. sample, when heated under reflux for one hour with 50 cc. of ethanol and 3 cc. of concentrated hydrochloric acid, gave 0.73 gm. (98%) of *trans*-cyclohexanediol with the proper melting point of 103° to 104°C., not depressed by admixture with an authentic specimen.

Method B with 0.1% hydrogen chloride and shaking for five days gave a product which was extracted with 100 cc. of low-boiling petroleum ether. Three recrystallizations of the residue from benzene recovered 54% of unchanged *trans* diol in a pure condition. The petroleum ether extract, when distilled at 23 mm. pressure, gave 3% of a colorless oil boiling at 76° to 78°C. and having the strong odor characteristic of the isopropylidene *trans* diol. Hydrolysis as described above removed the isopropylidene group and left 2.2% of the *trans* diol, whose purity and identity were confirmed by a mixed melting point. A similar condensation, employing 1% hydrogen chloride in acetone, yielded 11% of volatile material, from which only 0.7% of the original *trans* diol was recovered after acid hydrolysis.

cis-Monobenzoyl-*cis-cis*-Isopropylidene Cyclohexanetriol

A solution of the acetal, 5 gm., in 15 cc. of chloroform, 15 cc. of pyridine, and 5 cc. of benzoyl chloride was worked up by customary methods after standing at room temperature for 24 hr. After five recrystallizations from ethanol, the melting point of the 3.5 gm. of product (43%) became constant at 101.5° to 103.5°C. The portion analyzed was sublimed at 0.02 mm. pressure and then melted at 103.5°C. Found: C, 69.2; H, 7.4%. Calcd. for $C_{16}H_{20}O_4$: C, 69.5; H, 7.3%. The benzoate was soluble in common organic liquids but not in water.

trans-Monobenzoyl-*cis-cis*-Isopropylidene Cyclohexanetriol

A repetition of the above benzylation with 5 gm. of the isomeric isopropylidene acetal yielded 7.4 gm. (92%) of crude product but large losses occurred during several recrystallizations from 50% aqueous ethanol. These recrystallizations yielded 1 gm. of white needles which failed to melt sharply, a typical observation being m.p. 71.5° to 76°C. Sublimation at 0.02 mm. pressure gave a sample with m.p. 72° to 75.5°C. Found: C, 69.5; H, 7.5%. Calcd. for $C_{16}H_{20}O_4$: C, 69.5; H, 7.3%. This monobenzoate, like its isomer, was soluble in organic liquids but not in water.

cis-Monomethyl-*cis-cis*-Cyclohexanetriol

A 2.5 gm. sample of *cis-cis*-isopropylidene-*cis*-cyclohexanetriol was dissolved in 20 gm. of methyl iodide and 5 gm. of freshly prepared, dry silver oxide was added. After being warmed under gentle reflux for eight hours, the mixture

was extracted twice with hot methanol. Hydrolysis of the isopropylidene ether contained in the filtered extract was brought about by adding 2 cc. of concentrated hydrochloric acid and by heating under reflux for one hour. Neutralization, filtration, and evaporation left a brown residue that distilled at 0.02 mm. pressure. The distillate soon solidified. After sublimation at 65°C. and 0.02 mm. pressure and two recrystallizations from petroleum ether the average yield was 1.0 gm. or 47%. Specimens were prepared from isopropylidene derivatives made from the cyclohexanetriol by each of the Methods A and B. Each of these specimens melted at 69.5° to 71°C. and a mixed melting point was not depressed. Found: C, 57.8; H, 9.4%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.7%. The monomethyl cyclohexanetriol was soluble in water, alcohol, benzene, and acetone but dissolved very sparingly in petroleum ether.

bis-(3,5-Dinitrobenzoate) of cis-Monomethyl-cis-cis-Cyclohexanetriol

The monomethyl ether, 0.752 gm., was heated under reflux with 3,5-dinitrobenzoyl chloride, 0.752 gm., and pyridine, 3.5 cc., for 30 min. Recrystallization of the product from 30 cc. of ethanol and 20 cc. of ethyl acetate left 0.5 gm. of pure product, m.p. 190°C. Found: C, 46.9; H, 3.5; N, 10.6%. Calcd. for $C_{21}H_{18}O_{13}N_2$: C, 47.2; H, 3.4; N, 10.5%. An attempt to crystallize the corresponding dibenzoate failed.

This compound was prepared by R. Y. Moir and was analyzed by Marie A. Moir.

trans-Monomethyl-cis-cis-Cyclohexanetriol

The substance was prepared from the corresponding isopropylidene derivative, 2.5 gm., as already described for the *cis*-monomethyl isomer, and in 57% yield. The clear, colorless gum, distilled at 66° to 67°C. at 2 mm. pressure, crystallized completely as white needles when kept *in vacuo* over phosphorus pentoxide. Unlike the *cis* isomer, the present product was extremely hygroscopic and the melting point of 36° to 37°C. had to be taken in a highly evacuated Pyrex tube of 3 mm. diameter. No depression was observed in a mixed melting point of samples prepared from isopropylidene cyclohexanetriols made by Methods A and B. Found: C, 57.1; H, 9.6%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.7%.

Determination of Rates of Oxidation

With Lead Tetraacetate

A stock 0.1 M solution of the tetraacetate in redistilled, aldehyde-free glacial acetic acid was prepared and standardized iodometrically with 0.02 N sodium thiosulphate according to the directions of Hockett and McClenahan (13). The oxidations were carried out, exactly as described by these authors (14), with 100 cc. volumes 0.00025 M with respect to the diol or triol and about 0.005 M with respect to the lead tetraacetate. Blanks were run and temperature controlled to $18.6 \pm 0.5^\circ\text{C}$. When *a* and *b* were the initial molar

concentrations of the tetraacetate and the glycol, the rate constant K for a second order reaction was given by

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

The data (Table II) fitted this equation up to consumptions of 0.89 and 0.22, 0.91, 0.91, and 0.15 moles of tetraacetate, respectively, per mole of *cis* and *trans* cyclohexanediol, *cis-cis-cis*, *cis-cis-trans*, and *cis-trans-cis* triol, the slower reactions not being followed to completion. The monoethers of the *cis-cis-cis* and *cis-cis-trans* triols consumed 0.94 and 0.97 moles of tetraacetate per mole in 23 hr. at $20 \pm 0.1^\circ\text{C}$. and 1.02, 1.05 mole after 50 hr.

With Sodium Periodate

The procedure was adapted from the oxidations of the cyclohexanediols by Price and Knell (24). Twenty cubic centimeters of a stock 0.02 M solution of recrystallized periodic acid was mixed in a 100 cc. volumetric flask with 5.0 cc. of 0.045 N sodium hydroxide and 54 cc. of distilled water. At 18.6°C . and zero time, 20 cc. of an aqueous solution containing 0.00030 mole of the cyclohexanediol or -triol was added and the solution (pH 11.6) was made up to the mark with water and rapidly mixed. After various times, 10 cc. aliquots were titrated for remaining periodate by Fleury and Lange's sodium arsenite - iodine method (10). The data fitted the second order rate equation until the molar consumptions by the *cis* and *trans* diols, the *cis-cis-cis*, *cis-cis-trans*, and *cis-trans-cis* triols were at least 0.63 and 0.24, 0.99, 0.41, and 0.51 moles of periodate, respectively.

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RELATIVE STABILITIES OF THE ISOMERIC CYCLOHEXANE-1,2,3-TRIOL TRINITRATES AND 1,2-DIOL DINITRATES¹

BY W. R. CHRISTIAN² AND C. B. PURVES

Abstract

Of the above trinitrates, the *cis-cis-cis* and the *cis-trans-cis* isomers melted at 70° and 88°C., respectively, but the racemic *cis-cis-trans* form remained as a colorless viscid oil. When dissolved in excess 0.105 *N* aqueous-alcoholic sodium hydroxide at 20°C., the *cis-cis-cis* isomer hydrolyzed most rapidly but formed least nitrite, and the solution developed most color. The same isomer evolved the smallest amount of oxides of nitrogen when kept at 106°C., but was more readily detonated by shock than was the *cis-trans-cis*-trinitrate. The relative reactivities toward alkali and heat of the much more stable *cis* and *trans*-cyclohexane-1,2-diol dinitrates, which melted at 24° and 18.5°C., respectively, were as described for the trinitrates, but their relative sensitivities to shock were no less. All five compounds were new.

Introduction

Although it is generally conceded that the explosive properties of an aliphatic nitrate increase with the number of nitrate groups, correlations between these properties and the details of chemical structure and reactivity are still highly incomplete. Much of the available information on chemical reactivity concerns the decomposition of various aliphatic nitrates in alkali, and the early work in this field was reviewed by Lowry, Browning, and Farmery (15). The cleavage of nitrate groups in alkali generally proceeded on both sides of the ester oxygen atom, ---O---NO_2 , to yield either the parent alcohol and nitrate, or nitrite together with the corresponding aldehyde or ketone. Nitroglycerine, for example, gave nitrate and nitrite; Berl and Delpy (2) found a glycerol dinitrate among the products, but no mononitrate or glycerol. Conventional hydrolysis to an alcohol dominated in acidic conditions, or when a reducing agent was present in the alkali. Lachman (12) confirmed these principles for nitrotartaric acid, and found that the amount of nitrite formed from nitromalic acid was independent of the temperature, of the concentration and excess of alkali, but varied with the solvent (13).

According to kinetic studies by Lucas and Hammett (16), the cleavages of *t*-butyl nitrate and of *t*-butyl chloride to the alcohol and isobutene in acid, neutral, and alkaline dioxane-water mixtures were so similar that the same mechanisms of solvolysis and elimination could be postulated. Although more benzyl alcohol was produced from benzyl nitrate than from benzyl chloride by solvolysis, the mechanisms were otherwise similar, with the exception that none was suggested for the redox cleavage producing benzaldehyde

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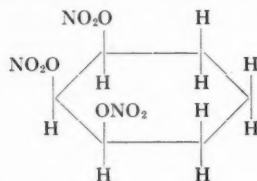
and nitrite from the benzyl nitrate. The hydrolysis of simple alkyl halides was also compared by Gand (8) with that of ethyl nitrate in neutral and slightly acidic systems containing potassium nitrate or silver iodide. Ethyl nitrate was observed to consume alkali more rapidly than its rate of hydrolysis would suggest. Other workers (9) found that the alkaline saponification of methyl-2,3,4-triacetyl- α -glucopyranoside-6-nitrate swiftly gave an almost quantitative yield of the methyl-3,6-anhydroglucoside, and that other mononitrates in the glucose series also yielded anhydro derivatives when the nitrate group could be eliminated by a mechanism of the Walden inversion type. When this mechanism was not available, as in methyl-2,3,4-trimethyl- β -glucoside-6-nitrate, saponification of the nitrate group was difficult, about 20% of nitrite was formed and the 2,3,4-trimethyl glucoside was recovered in about 75% yield. The other organic product was a resin presumably derived from trimethyl glucoside whose primary alcohol group had been oxidized to an aldehyde unit. Since these results were qualitatively the same as those obtained by saponifying halides and sulphonates in the sugar series, the analogy between aliphatic nitrates, halides, and sulphonates was strengthened. This analogy made it very probable that the mechanisms of elimination, solvolysis and substitution, described for halides and sulphonates in a series of articles by Winstein and his collaborators (24), would eventually find their counterparts for nitrate esters. The particular mechanism favored in a given reaction often depended upon the details of *cis-trans* isomerism and other spatial relationships.

The slow thermal decomposition of several simple aliphatic nitrates gave as principal initial products nitrogen dioxide and the aldehyde or ketone corresponding to the original nitrate (6), the final products from methyl nitrate containing nitric oxide and formaldehyde (1) or carbon dioxide, water, and nitrogen after explosive decomposition (25). Nitroglycerine yielded nitrogen dioxide as an initial product (22), and later work confirmed the fact that first order kinetics were obeyed (1, 21, 23); control experiments with added nitrogen dioxide, nitric acid, or moisture showed that the reaction was catalyzed by its products (23). The initial thermal decomposition of aliphatic nitrates thus appeared to resemble one of the mechanisms of saponification in being a redox reaction leading to carbonyl compounds and the elements of nitrous acid, including nitrogen dioxide.

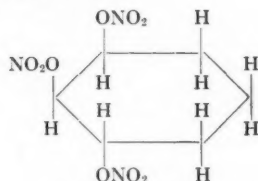
As a result of calculations based on dipole moments, de Kreuk (5) concluded that liquid nitroglycerine existed as various *cis-trans* conformations originating in free rotation about the carbon-carbon bonds and in proportions depending on the solvent. A consideration of the forces of repulsion existing between the nitrate groups suggested that the *cis-cis-cis* would be less stable than the *cis-trans-cis* conformation by an energy factor equivalent to 6330 cal. per mole. The all-*cis* conformation was then tentatively assigned to nitroglycerine in the "labile" crystal habit melting at 2°C., because Hibbert and Fuller (11) had shown that the spontaneous change of this form to the "stable" type of melting point 12.8°C. caused the evolution of practically the same amount of

heat, 6356 cal. The "stable" crystals were more sensitive to detonation by shock than the lower melting form, but results for liquid nitroglycerine were conflicting (7, 10, 11). This irregularity might possibly have been caused by the occlusion in the nitroglycerine of varying numbers of extremely minute gas bubbles (3). The "stable" allotrope had the greatest brisance (7), but the difference between the rates of detonation of the two crystal forms was small (7, 10). Explosion of 1 gm. of the "labile" crystals, on the other hand, produced more gaseous products, 560 cc., than the amounts, 518 cc. and 390 cc., obtained from the "stable" type and liquid nitroglycerine, respectively (7). If de Kreut's inferences were valid, *cis-trans* relationships between nitrate groups produced differences in explosive properties, either in a direct way, or indirectly through their effect on spatial relationships in crystal lattices.

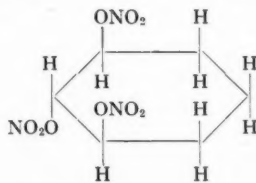
Recent researches (4, 17) accumulated supplies of the three isomeric cyclohexane-1,2,3-triols and made it possible to assign the proper stereochemical configuration to each. The present article describes the behavior of the three corresponding trinitrates, and also of *cis*- and *trans*-cyclohexane-1,2-diol dinitrates, toward alkali, together with some observations on their explosive properties. These trinitrates (structures I, II, and III) were regarded as conformations of nitroglycerine that were rendered capable of independent existence because the presence of the cyclic structure abolished, or very greatly restricted, free rotation about the carbon-carbon bonds.



I. *cis-cis-cis*
(γ -Pyrogallitol trinitrate)



II. *cis-cis-trans*
(β -Pyrogallitol trinitrate)



III. *cis-trans-cis*
(α -Pyrogallitol trinitrate)

Experimental

cis-cis-cis-Cyclohexane-1,2,3-triol Trinitrate

A 5 gm. sample of the pure *cis-cis-cis* triol, melting correctly at 148°C., was added slowly, at 0°C. with stirring, to 20 parts by weight (67 cc.) of 98% nitric acid in which 15 gm. of phosphorus pentoxide had been dissolved. After one hour at 0°C. the mixture was stirred into 1 liter of ice and water, and several

hours later the product was recovered, washed free of acid, and dried. Yield, 8.5 gm., or 84%; melting point 73° to 74°C. Recrystallizations from hot ligroin caused the material to separate as large thin plates belonging to the monoclinic, or possibly the triclinic, system, and melting at 74° to 74.5°C. Other organic liquids dissolved the substance freely at room temperature. Calc. for $C_6H_9N_3O_9$: C, 27.0; H, 3.4; N, 15.7%. Found: C, 26.9, 27.1; H, 3.8, 4.0; N(Dumas), 15.6, 15.7%; N(micro-Kjeldahl), 15.6, 15.7%.

Similar crude yields resulted in this case when the phosphorus pentoxide was omitted from the nitration mixture; also when the latter was replaced with glacial acetic acid, 100 cc., acetic anhydride, 38 cc., and 98% nitric acid, 18 cc. Nitrations with this mixture lasted from 15 min. to 16 hr. without influencing the yield.

cis-cis-trans-Cyclohexane-1,2,3-triol Trinitrate

A similar nitration of 5 gm. of the pure *cis-cis-trans* triol, melting correctly at 123.5° to 124.5°C., yielded an oil which was made acid-free by repeated washing in distilled water near 0°C.; the oil being recovered on the centrifuge after each wash. A solution of the oil in ether was decolorized with absorbent carbon, was dried over anhydrous sodium sulphate, and was evaporated under reduced pressure. After being kept *in vacuo* over phosphorus pentoxide, 7.6 gm. (75%) of a clear, very faintly yellow oil remained with a refractive index of n_D^{21} , 1.4895. Calc. for $C_6H_9N_3O_9$: N, 15.7%. Found: N, 15.6, 15.6%.

The substance showed no tendency to crystallize from solvents, nor after being kept for six months at -5°C. It was a colorless glass at -40°C.

cis-trans-cis-Cyclohexane-1,2,3-triol Trinitrate

A similar nitration of the pure *cis-trans-cis* triol, melting correctly at 109° to 110°C., was for one hour at -5°C. The crude product (66% yield and m.p. 83° to 84°C.) when recrystallized from hot ligroin yielded large rodlike prisms of either the monoclinic or triclinic systems and melting at 88° to 88.5°C. Calc. for $C_6H_9N_3O_9$: N, 15.7%. Found: N, 15.8, 15.6%.

cis-Cyclohexane-1,2,-diol Dinitrate

The pure *cis* diol, 10 gm. of m.p. 99°C., when nitrated at -5°C. for 30 min. gave an oil which was washed and dried as described above for the *cis-cis-trans* triol trinitrate. The product, 14.7 gm. or 83%, melted at 23° to 25°C., but wasteful recrystallizations from hot ligroin were necessary to yield the pure substance as prismatic rods with melting point 24.5° to 25°C. and refractive index, n_D^{21} , 1.4790. Calc. for $C_6H_{10}N_2O_6$: N, 13.6%. Found: N, 13.4, 13.4%.

trans-Cyclohexane-1,2,-diol Dinitrate

The pure *trans* diol, m.p. 104°C., when nitrated as described for the *cis* isomer, gave an 80% yield of an oil which crystallized as small irregular plates,

m.p. 17° to 19°C. Recrystallization from hot ligroin reduced the yield of pure material to 56% melting at 18.5° to 19°C. Calc. for $C_6H_{10}N_2O_6$: N, 13.6%. Found: N, 13.5, 13.6%.

Decomposition of the Nitroxy cyclohexanes in Alkali

In all cases the solvent was 50% aqueous ethanol by weight, or 60 parts of 95% ethanol to 40 parts of water by volume, the mixtures used being free of acidic impurities and dissolved carbon dioxide.

The experiments with the trinitrates were carried out at $20 \pm 0.05^\circ\text{C}$. in 100 cc. volumetric flasks containing 0.001 mole of each nitrate, and zero time was taken as the moment when the addition of 25 cc. of 0.4184 *N* aqueous-alcoholic sodium hydroxide brought the original solution up to the mark. The solution was promptly and thoroughly mixed. After various times 10 cc. aliquots were made acid by adding 25 cc. of 0.045 *N* hydrochloric acid, and the excess was back-titrated with 0.01013 *N* sodium hydroxide to pH 8.0. A Coleman pH meter was used because of the marked color of certain of the solutions (Figs. 1 and 2).

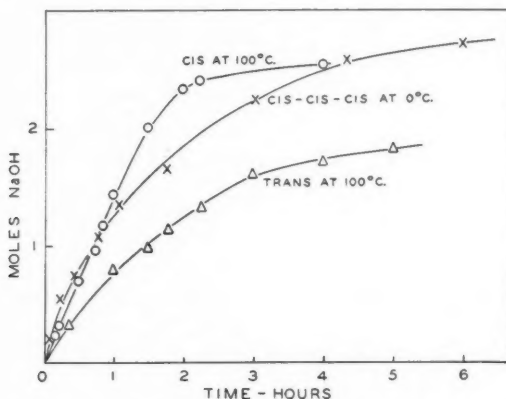


FIG. 1. Rate of neutralization of 0.105 *M* sodium hydroxide by 0.01 *M* solutions of the 1,2-dinitroxy cyclohexanes at 100°C., and of the *cis-cis-cis*-1,2,3-trinitroxy derivative at 0°C. Solvent, 50% aqueous ethanol.

Since the dinitrates reacted only very slowly at 20°C., they were examined at 100°C. The initial solution of 100 cc. was promptly divided into 10 cc. aliquots, each of which was contained in a 4 oz. bottle fitted with a screw top and a rubber gasket. The bottles were then heated in a steam oven for various times, were cooled, and the contents titrated as before. Blanks run without the nitrate showed that the glass of the bottles neutralized up to 3.7 cc. of the 0.01 *N* alkali as the time of heating was extended to five hours, but the corresponding plot, a reversed S in shape, was used to correct the results (Fig. 1).

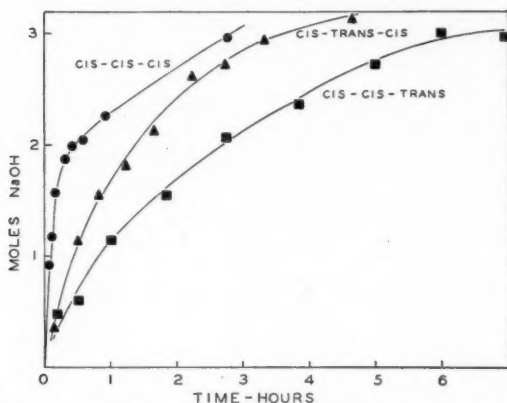


FIG. 2. Rate of neutralization of 0.105 *M* sodium hydroxide by 0.01 *M* solutions of the 1,2,3-trinitroxy-cyclohexanes at 20°C. Solvent, 50% aqueous ethanol.

After the titration to pH 8, each aliquot was diluted to 100 cc. and examined for color and nitrite content. The latter was determined by adding 1 cc. of Miller's (20) dimethylaniline-hydrochloric acid reagent to 25 cc. of the solution and estimating the depth of color produced by the yellow nitroso derivative four hours later. A photoelectric colorimeter with a blue filter was used, and the details of the technique were as described elsewhere (9). The blanks consisted of other 25 cc. volumes of each original solution adjusted to approximately the same pH with 1 cc. of 5 *N* hydrochloric acid instead of with 1 cc. of Miller's reagent. Known, accurate dilutions of pure 0.028 *M* sodium nitrite were used to establish the calibration plot and a plot of log per cent transmission of light against the concentration of nitrite was linear within the range studied, as was expected (9). Figs. 3 and 4 summarize the results.

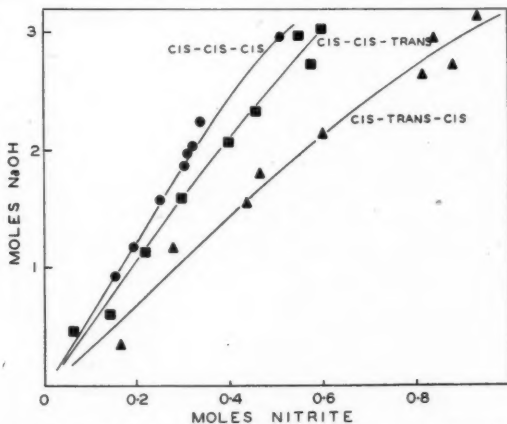


FIG. 3. Plots of moles nitrite formed against moles of sodium hydroxide neutralized by the solutions of the 1,2,3-trinitroxy-cyclohexanes at 20°C.

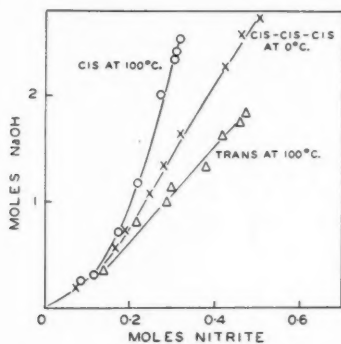


FIG. 4. Plots of moles nitrite formed against moles of sodium hydroxide neutralized by the solutions of the 1,2-dinitroxy cyclohexanes at 100°C., and of the *cis-cis-cis*-trinitroxy derivative at 0°C.

The remainder of each neutralized, diluted aliquot was then examined for its content of yellow color, the photoelectric calorimeter being used with a blue filter against distilled water as the standard. As the nature of the coloring material was unknown, it was necessary to assume that the amount was proportional to the intensity of color, and the plots in Fig. 5 were based on this assumption. No determinations were made with the cyclohexanediol dinitrates, both of which yielded solutions whose yellow-brown colors were much less intense than those from the trinitrates. As the intensity varied with the pH, a 10 cc. aliquot of the completely hydrolyzed *cis-cis-trans*-trinitrate was diluted to 100 cc. and acidified, when it became nearly colorless. The pH was then varied from 2.2 to 9.4 by the cautious addition of increments of concentrated sodium hydroxide, the over-all volume change being less than

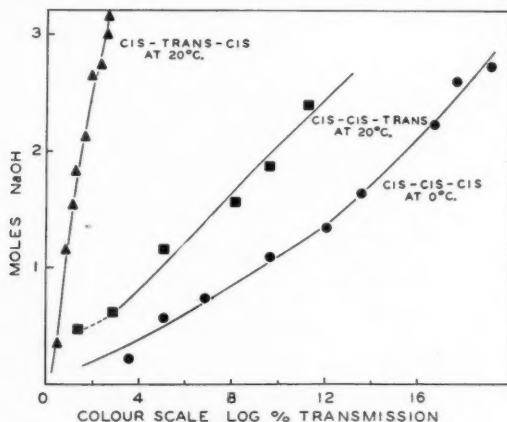


FIG. 5. Plots of moles sodium hydroxide neutralized against intensity of color produced in the solutions of the *cis-trans-cis* and *cis-cis-trans*-1,2,3-trinitroxy cyclohexanes at 20°C., and of the *cis-cis-cis* isomer at 0°C.

5%. A plot of the pH against the log per cent transmission of light formed a smooth curve slightly convex to the pH axis and showed that the action of pH was reversible within the limits cited.

Sensitivity to Impact

These tests were made on the Rotter Impact Machine, in which a blow caused by a steel ball falling from a variable height was communicated to the sample resting on a steel anvil. The minimum height required to produce detonations in 50% of the runs was found by trial and was compared with the corresponding heights for nitroglycerine and for trinitrotoluene, which were standard substances. The results are in Table I.

TABLE I
EXPLOSIVE PROPERTIES OF THE DI- AND TRINITROXYCYCLOHEXANES*

Substance	M.p., °C.	Drop test,** cm.	Ignition test		Bergmann-Junk test,† mgm. NO/gm.
			Fumes, °C.	Ignition, °C.***	
Dinitrates					
<i>cis</i>	24.5	A (300)		
<i>trans</i>	19	B 60	170	0.27
		A 85			0.67
		B 72	165	185	
Trinitrates					
<i>cis-cis-cis</i> ††	74.5	A 55			
		B 60	155	180	0.95
		C 60	170	182	
<i>cis-cis-trans</i> ††† (an oil)		A 40			
		B 34	155		3.5
		C 38	163	172	
<i>cis-trans-cis</i>	88.5	A 85			
		B 85	155	8.6

* Samples used in Tests A were retested four months later (Series B). Samples prepared four years later by Mr. N. S. Whittall were used for Tests C.

** Height of fall of steel ball required to produce detonation. Nitroglycerine, 8 cm.; trinitrotoluene, 100 cm.

*** Definite but mild explosions.

† After 20 hr. at 106°C. and atmospheric pressure. From data in Fig. 6.

†† A 6-gm. sample gave 1.23 times the power of trinitrotoluene in the ballistic mortar test.

††† A 6-gm. sample 1.28 times as powerful as T.N.T. in the ballistic mortar test.

Thermal Stability

The Bergmann-Junk-Mayrhofer (18, 19) method was used, the 0.1 gm. samples being heated at $106 \pm 1^\circ\text{C}$. for various times and the liberated oxides of nitrogen absorbed in 10 cc. of 5% potassium iodide. The equivalents of iodine liberated per mole of sample were estimated with 0.01 *N* sodium thiosulphate and were plotted against the time of heating (Fig. 6). Table I contains the results after heating for 20 hr., expressed as mgm. nitric oxide per gram sample.

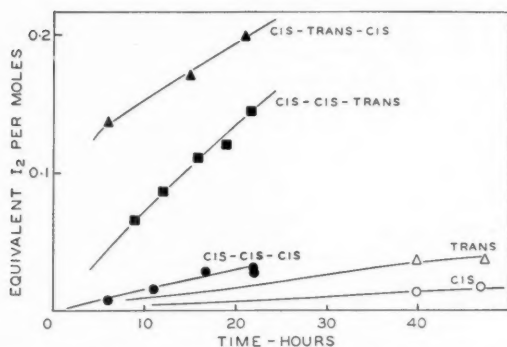


FIG. 6. Rates of evolution of oxides of nitrogen, expressed as equivalents of iodine per mole, from the 1,2,3-trinitroxy and 1,2-dinitroxy cyclohexanes when kept at 106°C.

Results and Discussion

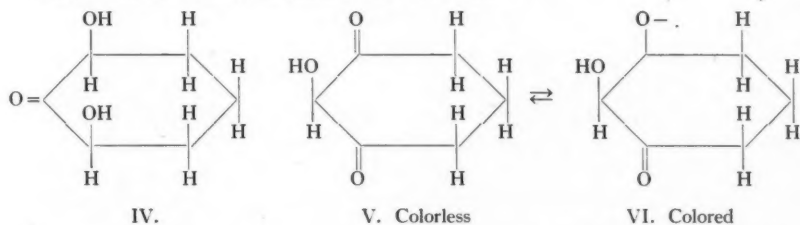
None of the five nitrates liberated an appreciable amount of acid when kept at room temperature in water, but all could be decomposed at convenient rates when dissolved in an excess of 0.105 *N* sodium hydroxide in 50% aqueous ethanol. The reactions were followed by noting the rate of disappearance of alkali, the rate of formation of nitrite, and the rate at which a yellow color developed in the solutions.

It is obvious from Fig. 1 that the *cis*-dinitrate (circles) neutralized more than the theoretical 2 moles of alkali, and reacted more rapidly than the *trans*-isomer (triangles); also that the rate for the *cis-cis-cis*-trinitrate at 0°C. (crosses) was comparable to that of the *cis*-dinitrate at 100°C. Multiplication of adjacent nitrate groups therefore greatly increased the over-all reactivity toward alkali. Results for the trinitrates at 20°C. (Fig. 2) showed that the *cis-cis-cis* isomer rapidly consumed nearly 2 moles of alkali and that the rate then diminished rather abruptly. Since the plot at 0°C. (Fig. 1) had no similar break, it appeared likely that the saponification proceeded by two reactions whose activation energies were different. The plot at 0°C. for the *cis-cis-cis*-trinitrate and that for the *cis-cis-trans* isomer at 20°C. happened to be almost superposable at all times up to five hours. By analogy with the results in Fig. 1, it was expected that the *cis-trans-cis*-trinitrate would be least reactive toward alkali, but this position was taken by the *cis-cis-trans* isomer (squares). The initial point on the *cis-cis-trans* plots in Figs. 2, 3, and 5 appeared displaced in the direction of a greater consumption of alkali, although the reaction of the original trinitrate toward water was neutral. An unknown, readily saponified impurity or a small amount of an *aci*-modification of the kind encountered by Gand (8) in ethyl nitrate, might have been present in this uncrystallized trinitrate, but the proper explanation was not determined.

The unexpected position of the *cis-trans-cis*-trinitrate in Fig. 2 was perhaps related to the superior amount of nitrite which this isomer produced (Fig. 3), and in this case the *cis-cis-trans*-trinitrate occupied the intermediate position.

Although these plots at 20°C. appeared to be linear, the mechanics of nitrite formation were probably complex because the data for the *cis-cis-cis* isomer at 0°C. clearly indicated a more extensive initial reaction (Fig. 4, crosses). The same type of plot was given by the *cis*-dinitrate at 100°C., and possibly by the *trans* isomer, which definitely produced more nitrite per mole of sodium hydroxide consumed. Since the plot for the *trans*-dinitrate at 100°C. was accurately superposable on that for the *cis-trans-cis*-trinitrate at 20°C., the mechanism of nitrite formation was probably independent of temperature and identical for both of these *trans* compounds.

It was noted that the color assumed by the alkaline solutions of the nitrates ranged in intensity from slight yellow-brown for the dinitrates at 100°C. to a clear, very deep yellow for the *cis-cis-cis*-trinitrate at 20°C. Fig. 5 shows that the intensity of color imparted by this trinitrate, even at 0°C., exceeded those given by the other two isomers at 20°C., and that the *cis-cis-trans*-trinitrate was once more in the intermediate position. These intensity measurements were all made at pH 8 because the depth of color decreased in a reversible fashion with pH. The assumption that the intensity of color was proportional to the amount of the color-producing substances led to the conclusion that the *cis-trans-cis*-trinitrate, which produced most nitrite and presumably the greatest amount of alkali-sensitive carbonyl compounds, nevertheless gave the smallest yield of colored products. The production of about 0.9 mole of nitrite from the three nitrate groups in the *cis-trans-cis* isomer might, however, have resulted in a 90% yield of a monoketone such as (IV), which would remain nearly colorless in alkaline solution. On the other hand, the 0.5 mole of nitrite released by the *cis-cis-cis*-trinitrate might correspond to the formation of 25% of a diketone of type (V), which would probably behave as an indicator yielding a colored charged particle (VI) in the higher pH range (14). A further breakdown of a diketone would also explain the high consumption of alkali by the *cis-cis-cis*-trinitrate (Fig. 2). These speculations are at present entirely unsupported by experimental evidence.



Submission of the five nitrates to a temperature of 106°C., as in the standard Bergmann-Junk test for the thermal stability of explosives, liberated oxides of nitrogen that were estimated as equivalents of iodine per mole of sample (Fig. 6). The *cis-trans-cis*-trinitrate proved to be the least stable, and was also distinguished by the failure of the plot to pass near the origin of the coordinates. The amounts of the oxides liberated thermally were in the same sense as the production of nitrite in the saponifications, both for the trinitrates

and for the much more stable *trans* and *cis* dinitrate. Table I, Column 5, expresses the decompositions after 20 hr. in the customary way as mgm. nitrous oxide per gm. sample. The ignition test (Table I) revealed little difference between the nitrates, but sensitivity to detonation by shock was definitely greater for the *cis-cis-cis*-trinitrate and *cis*-dinitrate than for the corresponding *trans* compounds. These results paralleled the rate and amount of alkali consumed by the nitrates (Figs. 1 and 2) and not the amount of nitrite formed during saponification. The *cis-cis-trans*-trinitrate, however, consumed less alkali than its isomers but was much more sensitive to shock. Although this trinitrate was an uncrystallized raceme, the unexpectedly high sensitivity could hardly be attributed to impurities or to the occlusion of gas, because a sample prepared four years later by another worker gave a concordant result. The explanation of this anomaly remained obscure. Since both the *cis* and *trans* dinitrates were molten when tested for sensitivity, the results must be attributed to their difference in molecular shape rather than to difference in crystal habit. The same inference might possibly be drawn for the all-*cis* and all-*trans* trinitrates, because their respective sensitivities duplicated those of the *cis* and *trans* dinitrates within the observational error.

As already mentioned, crystalline nitroglycerine of the "stable" type was more sensitive to detonation by shock than the "labile" isomer. Analogy with the present work suggests that the respective conformations would be *cis-cis-cis* and *cis-trans-cis*, but de Kreuk's arguments reversed this assignment. The superior over-all reactivity of the *cis-cis-cis*-cyclohexanetriol trinitrate toward alkali was unexpected in the light of the general chemical behavior of halide, acetyl, or sulphonyl substituents (24), and the mechanisms underlying sensitivity and thermal stability obviously depended in different ways on *cis-trans* configurations. It was unfortunate that the comparative inaccessibility of the *cis-cis-trans*, and the great inaccessibility of the *cis-trans-cis*, cyclohexane-1,2,3-triols prevented a closer study of these problems.

Acknowledgments

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AN IMPROVED SYNTHESIS OF *CIS-CIS-TRANS*-CYCLOHEXANE-1,2,3-TRIOL¹

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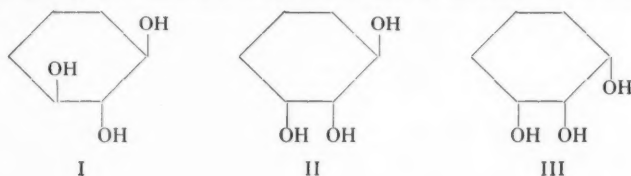
Abstract

Cyclohexene-3-ol acetate was readily made from cyclohexene and when oxidized, preferably with performic acid, gave 20 to 25% yields of partly acylated *cis-cis-trans*-cyclohexane-1,2,3-triol, but only 1 to 2% of the *cis-trans-cis* isomer. The structures of the three cyclohexane-1,2,3-triols were deduced from the theory of the Walden Inversion.

Introduction

In a previous article (9) it was shown that *cis-cis-cis*-cyclohexane-1,2,3-triol (γ -pyrogallitol) was readily obtained in about 60% yield by the high-pressure hydrogenation of pyrogallol, but that this method gave unsatisfactory amounts of the *cis-cis-trans* and *cis-trans-cis* isomers (β - and α -pyrogallitols). Moreover, the separation of these isomers by fractional crystallization from the preponderating *cis-cis-cis* form was tedious and wasteful. The object of the present work was to employ cyclohexene as a starting material for an independent synthesis of the less accessible isomers.

Lindemann and de Lange (23) obtained and carefully characterized all three of the possible cyclohexane-1,2,3-triols from the hydrogenation of pyrogallol; two of these isomers had previously been made from cyclohexene and accurately described by Brunel (8), and the third had been made by Senderens and Aboulenc (34). Assignment of the correct stereochemical structure to each of the isomers proved difficult. Since the triol with structure II is the only one



which is resolvable, Lindemann and de Lange (23) converted each of the triols into its *l*-menthylurethane in an attempt to find the resolvable form. The α -triol and the γ -triol each gave single products, while the β -triol gave an oil whose failure to crystallize was thought to be due to the presence of diastereoisomers. Hence they assigned structure II to the β -triol. Posternak and Ravenna (31) by attacking each of the isomers with micro-organisms which oxidized

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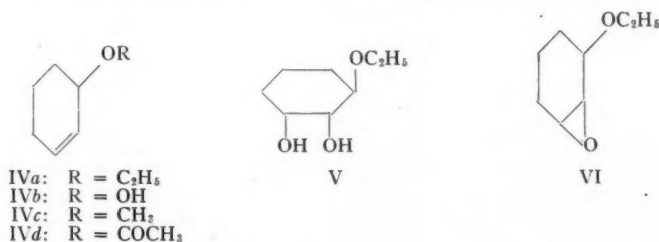
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cis glycols in preference to *trans* glycols, were able to show that the α -isomer, m.p. 108°C., had structure I, that the β -isomer, m.p. 124°C., had structure II and was resolvable into optical isomers, and that the γ -isomer, m.p. 148°C., had structure III. This assignment of structures was confirmed, both by Posternak and Ravenna (31) and by Christian, Gogek, and Purves (9), by measuring the rate at which each of the triols reacted with lead tetraacetate.

It is also possible to deduce the structures of the triols from Brunel's syntheses by means of recent developments in the theory of the Walden Inversion. This in part was done by Posternak and Ravenna; a more complete analysis is now given. The following rules, which are based upon the theory and which have been repeatedly verified by experiment, are employed: (1) oxidation of an olefin with potassium permanganate gives a *cis* glycol (3, 5, 32); (2) dealkylation of an alkyl ether with hydrobromic acid does not cause inversion of configuration (16, 19, 21, 24, 30); (3) when a nucleophilic reagent attacks an ethylene oxide ring, the carbon of the ring which retains the oxygen atom is not inverted, but the carbon of the ring which is attacked by the reagent is inverted (2, 3, 29). When Brunel (8) oxidized 3-ethoxycyclohexene (IVa) with potassium permanganate and treated the resulting syrupy glycol (V) with hydrobromic acid, he obtained only the β -cyclohexane-1,2,3-triol, m.p. 124°C., so that the β -triol must have two neighboring hydroxyl groups in the *cis* position to each other (Rules 1 and 2). Brunel formed also from 3-ethoxycyclohexene (IVa) the oxide VI, probably as a mixture of stereoisomers. When the oxide was heated with water, mixed ethoxydiols were produced, and when



these ethoxydiols were heated with hydrobromic acid, both the α -triol, m.p. 108°C., and the β -triol, m.p. 124°C., were obtained. Each of these triols must have a pair of neighboring hydroxyl groups in the *trans* position to each other (Rules 2 and 3). Therefore the β -triol which contains a pair of neighbors in the *cis* position, and a pair in the *trans* position, must be II; the α -triol must be I, and the γ -triol, not formed in the reactions, must be III. Further, one might conclude that the ethoxydiol of Brunel, and the 3-ethoxycyclohexane-1, 2-diol, m.p. 28°C., of Hofmann and Damm (18), made by the permanganate oxidation of 3-ethoxycyclohexene, must have structure V. It may be added that substantially the same analysis of the situation was first made by one of us (27) in 1944, independently of any of the other determinations of structure already mentioned.

Two exceptions are known to the third rule (that the ethylene oxide ring is opened with one inversion of configuration). The first, involving the acid hydrolysis of 1-phenylcyclohexene oxide (5) is a striking confirmation of the mechanism proposed by Kadesch (1, 20) for the 'abnormal', acid-catalyzed reactions of certain oxides which can have an intermediate carbonium ion stabilized by resonance. The second (28), involving the two-step conversion of 2-acetyl-6-trityl-3:4-anhydro- α -methylgalactoside into a galactose derivative, that is, with an over-all retention of configuration, is an equally striking illustration of Winstein's 'neighbor' mechanism (40). Ordinarily after an oxide ring has been opened by inversion, subsequent reactions of the resulting groups take place without inversion of configuration because of the presence of a neighboring group in the *trans* position, but in this example from the work of Oldham and Robertson (28) neither neighboring group can participate, one because it is in the *cis* position with respect to the attacked center, the other because it is already tied up in a cyclic acetal ring. Thus two successive inversions occur with over-all retention of configuration. Neither of these exceptional reactions disturbs in any way the application of the rule to simple oxides such as those under discussion in this paper.

A modification of Brunel's synthesis of the α - and β -triols was first investigated as a method of producing these triols in quantity. The starting material, 3-methoxycyclohexene (IVc) had been made and characterized by Brunel (7) and during the course of our work was also made by Berlande (4), but it is much more conveniently prepared in quantity by the action of sodium methylate upon cyclohexene dibromide—a method used by Hofmann and Damm (18) for the production of 3-ethoxycyclohexene (IVa). Oxidation of the 3-methoxycyclohexene with peracetic acid by the method of Scanlan and Swern (32) gave a syrupy mixture of the 3-methoxycyclohexane-*trans*-1,2-diols, and this mixture when treated with hydrobromic acid yielded a mixture of the α -cyclohexanetriol (I) and the β -cyclohexanetriol (II) in almost equal amounts, but in low yield. Although disappointing from the preparative point of view, this synthesis served to confirm the structure of the 3-methoxycyclohexene made by the method of Hofmann and Damm. Since olefins are oxidized to *trans* glycols by peracids (5), it also confirmed the structure of the γ -triol (III) by a method more direct than the triol synthesis of Brunel.

Better results were obtained by synthetic routes which employed 3-acetoxycyclohexene (IVd) as an intermediate. A methylene group in the allylic position in cyclohexene is vulnerable to attack by such reagents as lead tetraacetate (11), selenium dioxide in acetic anhydride (15), chromic anhydride in acetic acid (37), diazonium compounds (38), oxygen in the presence of osmium (39) or in the presence of ultraviolet light (12, 14), mercuric acetate (6, 36), and *N*-bromosuccinimide (41). Farmer and Sundralingam (14) and Kötzt and Richter (22) both used cyclohexene hydroperoxide (IVb) as an intermediate in the synthesis of mixtures of the cyclohexanetriols; Farmer and Sundralingam isolated the pure β -triol (II) from the mixture obtained by them. However, the first two methods seemed more practical to us. Criegee's yield

of 21% of 3-acetoxycyclohexene (IVd), from the oxidation of cyclohexene with lead tetraacetate (11), was confirmed, but for larger-scale work, Guillemonat's oxidation with selenium dioxide (15) was found preferable even although his yield of 45% could not be reproduced. Three preparations made according to his instructions each gave close to 19% of the uncrystallized but redistilled acetoxycyclohexene, together with 0.4% of cyclohexenone, whereas Guillemonat's recovery of the latter was 10%. Saponification of the acetate gave a 68% yield of 3-hydroxycyclohexene, with the correct boiling point. No previous value for the yield was found in the literature.

The hydroxylation of the 3-acetoxycyclohexene was carried out by three methods, the first of which employed tertiary-butyl peroxide with selenium dioxide as a catalyst (33); the second, hydrogen peroxide in sulphuric and glacial acetic acids (25), and the third, hydrogen peroxide in formic acid (35). In each instance acyl groups were removed from the distilled but uncrystallized product by saponification, and the resulting mixture of crude triols was separated by fractional crystallization of the tribenzoates. The yields of the pure *cis-cis-trans*-cyclohexanetriol (II) tribenzoate were 24.6%, 22.9%, and 20 to 25% for the three methods of preparation, but the corresponding figures for the *cis-trans-cis* tribenzoate (of the α -triol) were only 2%, 0.5%, and 1%. Although for convenience the performic acid method was preferred, the results strongly suggest that the factor dominating the mode of *trans* addition to the double bond was not the conditions of the hydroxylation with peroxide but rather the presence of the acetoxy group. This group appeared in the product overwhelmingly in the *cis* relationship to the adjacent hydroxyl group and in consequence the synthesis offers a reasonably satisfactory preparation for the *cis-cis-trans*-, but not for the *cis-trans-cis*-cyclohexanetriol.

Experimental

Materials

Cyclohexene, boiling correctly at 82° to 84°C., was prepared by Coleman and Johnstone's procedure (10). The selenium dioxide was a high grade sample generously given by Canadian Copper Refineries Ltd., Montreal.

3-Cyclohexenol Acetate

Guillemonat's procedure (15) was closely followed, the quantities used being 820 gm. of cyclohexene (10 moles), 500 gm. of acetic acid, 300 gm. of acetic anhydride, and 389.5 gm. of finely powdered selenium dioxide (3.5 moles). Steam distillation of the product recovered 140 gm. of cyclohexene and 92.4 gm. of 3-cyclohexenol acetate boiling at 81° to 83°C. at 25 mm. pressure.

When heated at 200°C. and 25 mm. pressure, the black still-residue yielded a brown distillate from which an additional 132 gm. of pure cyclohexenol acetate was eventually recovered, thereby raising the total yield to 224.4 gm. or 19.3% of theory. The same crude distillate on extraction with 40% aqueous sodium bisulphite yielded 3.1 gm. (0.4%) of 2-cyclohexenone with the correct

boiling point of 65° to 67°C. at 24 mm. pressure. Guillemonat's yield was 10%. Cautious treatment of the final still-residue with concentrated nitric acid recovered almost all of the selenium dioxide used.

The acetate was saponified by shaking with an equivalent amount of aqueous barium hydroxide for one hour, the product being extracted from the liquors with benzene. A 68% yield of material boiling at 60° to 62°C. at 12 mm. was obtained. Guillemonat's product boiled at 67°C. at 15 mm. pressure.

Cyclohexene-1,2,3-triols from 3-Cyclohexenol Acetate

(a) By Seguin's method (33). The acetate (79.7 gm. or 0.57 mole) and selenium dioxide (2.3 gm.) were added to a solution of 0.58 mole of hydrogen peroxide in 275 cc. of tertiary butyl alcohol (17, 26). After a few minutes' shaking, all of the oxide dissolved and the solution was kept at 6°C. for six days. Distillation *in vacuo* first removed the butyl alcohol, then 22.7 gm. of unchanged cyclohexenol acetate and 31.3 gm. of a light yellow gum containing a trace of red selenium. The viscous black still-residue contained carboxylic acids. The gum, which boiled at 120° to 130°C. at 0.05 mm. pressure, was saponified at room temperature with 10.1 gm. of potassium hydroxide in 125 cc. of methanol and the alkali was subsequently removed as the chloride. Evaporation and distillation of the mother liquor at 0.2 mm. pressure yielded 24.8 gm. (44%, based on unrecovered cyclohexenol acetate) of crude, semi-solid cyclohexanetriols. Benzoylation of this product gave 63.0 gm. of crude tribenzoates which were separated by fractional crystallization (9) into 45.4 gm. (24.6%) of the pure *cis-cis-trans* form, m.p. 182°C., and 3.7 gm. (2%) of the *cis-trans-cis* isomer melting correctly at 140°C. The mother liquors yielded further small amounts in a less pure condition.

(b) By the method of Meerwein, Schoeller, Schwenk, and Borgwardt (25). A solution containing 44.7 gm. of hydrogen peroxide (30%, 0.395 mole), 44.7 gm. of glacial acetic acid and 4.6 gm. of concentrated sulphuric acid, was added to 50 gm. (0.36 mole) of 3-cyclohexenol acetate during one hour. The mixture became homogeneous after being stirred at 10° to 15°C. for five hours, and after 56 hr. at this temperature was kept at 40° to 50°C. for three hours. Two layers appeared when the solution was neutralized exactly with sodium hydroxide, and the upper layer was combined with a benzene extract of the lower aqueous phase. Evaporation of the aqueous phase to dryness, followed by extraction of the residue with acetone, eliminated inorganic salts. The benzene and acetone extracts were then combined and on fractional distillation gave 3.1 gm. of unchanged cyclohexenol acetate and 29 gm. of a light yellow gum boiling at 120° to 127°C. (0.05 mm. pressure). Saponification of this gum gave a brown, salt-free residue of which 13.7 gm. was volatile at 130° to 132°C. (0.08 mm. pressure). When benzoylated, this fraction eventually yielded 34.8 gm. of pure *cis-cis-trans*-cyclohexanetriol tribenzoate (m.p. and mixed m.p. correct at 183°C.) and 0.8 gm. of the *cis-trans-cis* isomer, m.p. 140°C. The over-all yields of the tribenzoates were 22.9% and 0.5%, respectively.

(c) By the method of Swern, Billen, Findley, and Scanlan (35). Hydrogen peroxide, 58.1 gm. (30%, 0.502 mole), was added during 15 min. to a mechanically stirred mixture of cyclohexenol acetate (70 gm., 0.50 mole) and 150 cc. of 87% formic acid. Initial cooling was used so that the temperature did not rise above 55°C., and after two or three hours heat was applied to maintain this temperature for a further 16 hr. The solution was then brown in color and had deposited a small amount of a dark resin. The residue left after removal of solvents yielded 53.2 gm. of a pale yellow distillate, boiling at 120° to 135°C. at 0.05 mm. pressure. Hydrolysis of this product with boiling water to remove formate followed by saponification with methanolic caustic potash to remove acetate groups, left 21.6 gm. of redistilled cyclohexanetriols. Benzoylation and fractional crystallization then recovered 45.6 gm. (20.0%) of the pure *cis-cis-trans*-tribenzoate and 2.5 gm. (1.1%) of the pure *cis-trans-cis* isomer. The crude acetate-formate from a second experiment employing the same amounts of reactants but in which the hydroxylation was for 24 hr. at room temperature, was hydrolyzed in one operation by heating for 90 min. at 50°C. with 3 cc. of concentrated sulphuric acid in 150 cc. of ethanol and 25 cc. of water. After recovery, the 36.3 gm. of crude distilled triols were shaken mechanically with ethyl acetate for an hour to extract 17.5 gm. (25%) of a yellow oil that boiled at 120° to 135°C. (0.15 mm.) and dissolved in benzene and ethanol but not in water. Although this oil was not examined in detail, the formation of a bright red precipitate with 2,4-dinitrophenylhydrazine indicated that it contained a carbonyl group. The remaining 18.6 gm. of the crude distilled triols yielded 11.5 gm. of pure *cis-cis-trans*-cyclohexanetriol (m.p. 125°C. and isolated as such) and a further 17.4 gm. of the pure tribenzoate, the total yield being 24.6%. Two grams of the pure *cis-trans-cis*-tribenzoate (0.9%) were also recovered.

3-Methoxycyclohexene and Cyclohexadiene

The method was that described by Hofmann and Damm (18) for 3-ethoxycyclohexene. Sodium, 71.3 gm., was dissolved in absolute methanol, 900 cc., and crude cyclohexene dibromide, 307 gm., was added. The mixture was refluxed for 10 hr., most of the methanol was distilled away, and the residue diluted with water, 2000 cc. Repeated extraction of the aqueous mixture with ether, followed by distillation of the dried ethereal extract gave 48.0 gm. of crude methoxycyclohexene. Further amounts of the crude product were obtained by repeated fractional distillation of the methanol distillate, so that the average over-all yield was 60%. When several of the crude preparations were carefully fractionated together, a very pure sample of 3-methoxycyclohexene, 278.4 gm., of b.p. 138.7°-138.8°C. (corr.) at 757 mm. (corr.) was obtained. Berlande (4) reported a b.p. of 139°C., and Brunel (7) a b.p. of 139.8°C. for 3-methoxycyclohexene. Cyclohexadiene was recovered in about 7% yield by diluting the lowest-boiling methanol fractions with water, followed by distillation of the insoluble oil. It was conveniently identified and preserved by converting it to the addition product with maleic anhydride, whose m.p. of 147°-147.5°C. agreed with that reported by Diels and Alder (13).

Hydroxylation of 3-Methoxycyclohexene

An adaptation of Scanlan and Swern's method (32) was used for the hydroxylation.

Glacial acetic acid, 250 cc., and 30% hydrogen peroxide, 70 cc., were thoroughly stirred and kept for one hour at 80° to 85°C. in order to form peracetic acid. After cooling the solution to 50°C., 42.7 cc. of methoxycyclohexene were added slowly from a dropping funnel, so that the temperature did not exceed 72°C., and the mixture was then kept at 65° to 70°C. for 1.75 hr. Reduction of the excess peroxide with magnesium metal and a little iron, followed by evaporation of the solution *in vacuo*, left a residue which was thoroughly extracted with ethyl acetate. Distillation of this extract yielded crude 3-methoxy-*trans*-cyclohexanediols as an almost colorless viscous oil boiling at 84° to 98°C. (0.025 mm. pressure). The yield of 17.4 gm. (about 30%) was probably diminished by the presence of inorganic salt during the distillation.

The dealkylation of this product was as described by Brunel (8) for the corresponding ethoxy compound; 9.9 gm. were kept with 11 cc. of hydrobromic acid (saturated with hydrogen bromide at 0°C.) in a sealed glass tube at 60°C. for 20 min. After recovery, the liquid was diluted with water, neutralized with sodium bicarbonate and evaporated to dryness. Distillation of an ethanol extract of the residue yielded 4.8 gm. (about 50%) of partly solid cyclohexanetriols boiling at 95° to 120°C. at 0.04 mm. A small amount, 0.6 gm., of crude *cis-trans-cis*-cyclohexanetriol separated when this mixture was diluted with acetone. Benzoylation of the residue, and fractional crystallization of the product (9) yielded 2.9 gm. each of the crude *cis-cis-trans*- (m.p. 153° to 180°C.) and *cis-trans-cis*-tribenzoates (m.p. 122° to 128°C.). Small amounts of both isomers were subsequently isolated with correct melting and mixed melting points (184° and 142°C., respectively) by tedious fractional recrystallizations. Both crude tribenzoates were recovered in an over-all yield of about 3% from the methoxycyclohexene and of about 10% from the methoxycyclohexanediols.

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THE BENZOATE AND THE METHYL ETHER OF 4-HYDROXYCYCLOHEXENE¹

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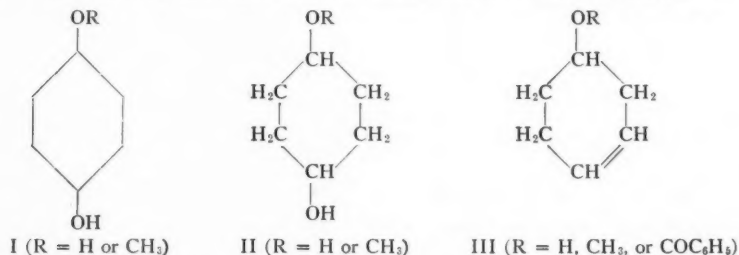
Abstract

Satisfactory preparations, from hydroquinone and its monomethyl ether respectively, were devised for the above compounds which were thought to be new. The methyl ether of 4-hydroxycyclohexene was an oil, n_D^{20} 1.4566, boiling at 136°C.; the uncrystallized benzoate had n_D , 1.5360 and b.p. 149°C. at 12 mm. pressure.

Introduction

The original objective of the work was to study the *cis-trans* isomerism of the four cyclohexane-1,2,4-triols, members of which have been prepared in crude form by Senderens and Aboulenc (7) and by Zelinsky and Titowa (9). Circumstances, however, made it necessary to discontinue the research after preparing 4-hydroxycyclohexene, its methyl ether, and its benzoate (structures III), any of which would yield one pair or another of the desired triols by a directed *cis* or *trans* hydroxylation of the double bond.

The high pressure hydrogenation of hydroquinone (I, R = H) over a Raney nickel catalyst gave up to 96% yields of crude, crystalline cyclohexane-1,4-diol (II, R = H, quinitol), the *cis-trans* isomers of which have been studied on several occasions (1, 2, 4, 5). Distillation of the quinitol over a little concentrated sulphuric acid (6) yielded the known substance 4-hydroxycyclohexene (III, R = H), the new monobenzoate of which was then readily prepared



Helfer's (3) methylation of hydroquinone gave a 40 to 44% yield of the crystalline monoether (I, R = CH₃), which on hydrogenation (3, 8) gave 66 to 83% yields of the methoxycyclohexanols (II). Dehydration of the latter resulted in the new compound (III, R = CH₃) in 58% yield.

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The molar refractivities found for 4-methoxycyclohexene (III, $R = CH_3$) and for cyclohexene-4-ol benzoate (III, $R = COC_6H_5$) were higher than expected. Our later experience with this general class of compounds has shown that they autoxidize at an unusually fast rate, so that the refractive indices here reported may be slightly higher than the correct values.

Experimental

Benzoate of 4-Hydroxycyclohexene

A solution, 1100 cc., of pure hydroquinone, 525 gm., in ethanol was hydrogenated over 80 gm. of Raney nickel catalyst at 170°C. and 3000 p.s.i., or substantially as recommended by Coops, Dieneske, and Aten (2). The product, boiling correctly at 140° to 143°C. at 8 mm., crystallized at once to 527.5 gm. (96%) of the mixed *cis* and *trans*-cyclohexane-1,4-diols. A 527.5 gm. sample of the diols, heated with 2 cc. of 65% sulphuric acid in a bath at 190° to 200°C. (6) yielded a distillate containing water, cyclohexadiene, and 168 gm. (38%) of crude 4-hydroxycyclohexene boiling at 154° to 157°C. Redistillation gave the pure substance with the correct boiling point of 164° to 165°C.

A cold solution of 87.2 gm. (0.89 mole) of the 4-hydroxycyclohexene in 200 cc. of pyridine was mixed with 128 gm. (0.91 mole) of benzoyl chloride diluted with 350 cc. of chloroform. The product, recovered after the mixture had remained for 16 hr. at room temperature, was twice distilled at 12 mm. pressure through a Vigreux column. Cyclohexene-4-ol benzoate was a colorless oil boiling at 149° to 150°C. (12 mm.); d_4^{20} , 1.083 and n_D^{20} , 1.5360. Found: C, 77.3%, H, 6.9%; mol. refraction, 58.23. Calcd. for $C_{13}H_{14}O_2$: C, 77.2%; H, 7.0%; mol. refraction, 57.64.

The benzoate was insoluble in water but soluble in benzene, alcohol, acetone, and chloroform. It decolorized dilute solutions of bromine in carbon tetrachloride, and of aqueous potassium permanganate, instantly.

4-Methoxycyclohexene

Hydroquinone, 660 gm., was methylated in two batches at room temperature with 574 cc. of technical dimethyl sulphate in presence of 600 gm. of sodium hydroxide and 3600 cc. of water (3). *p*-Dimethoxybenzene, 130.8 gm., was separated by filtration, and, after recovery, the *p*-methoxyphenol remained as a light brown oil boiling at 118° to 130°C. at 8 mm. pressure. The distillate rapidly solidified to crystals melting at 55° to 57°C.; yield, 330.6 gm. or 44%. Helfer (3) obtained a 55% yield of material melting at 53°C. The high pressure hydrogenation of the *p*-methoxyphenol, 771.8 gm., with 100 gm. of Raney nickel catalyst was as described by Van Duzee and Adkins (8) and proceeded rapidly at 180° to 190°C. An 83% yield (665.7 gm.) of crude 4-methoxycyclohexanol boiling in the range 85° to 120° (7 mm. pressure) was obtained.

A total of 603.6 gm. of this crude product was distilled at 205°C. in three batches, each containing about 2 cc. of 50% sulphuric acid (6). Redistillation yielded first a mixture (91 gm.) of water with cyclohexadienes and then 257 gm.

of pure 4-methoxycyclohexene boiling at 135.5° to 136.5°C. (760 mm.). Re-distillation of the still residue with an additional 2 cc. of 50% sulphuric acid produced an additional 42.0 gm. of pure material and increased the yield to 58%.

4-Methoxycyclohexene was a colorless oil with d_4^{20} , 0.9009 and n_D^{20} , 1.4566. Found: C, 74.7%; H, 10.4%; mol. refraction, 33.89. Calcd. for $C_7H_{12}O$: C, 74.9%. H, 10.8%; mol. refraction, 33.54. The compound was soluble in organic liquids but not in water, and instantly decolorized bromine in carbon tetrachloride, or dilute aqueous potassium permanganate.

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THE ROLE OF ALPHA-KETOLS IN THE LOW-SUGAR REDOX RECIPE FOR LOW TEMPERATURE EMULSION COPOLYMERIZATION¹

BY R. J. ORR AND H. LEVERNE WILLIAMS

Abstract

It was found that the induced decomposition of peroxy compounds could lead to faster rates of polymerization or practical rates of polymerization at lower temperatures. In Germany polymerization recipes were developed containing a peroxy compound in the oil phase, a reducer in the aqueous phase and a metal carrier. This idea was transferred to America after the war and became the basis of the present recipes used in the production of cold rubbers. As reducers the most commonly used appear to be digested *d*-glucose or an excess of ferrous iron but recently the polyamines and other amine compounds have been found to be quite effective. The mixture of amine and sugar was better than either alone. It has been shown that this mixture will function in the presence of reactive monomers such as acrylonitrile. The role of such reducers is of considerable interest so that further studies were undertaken. The results obtained may be illustrated by acetoin. As the amount of acetoin is increased in the recipe the amount of ferrous iron required for maximal conversion in a given time is decreased. This is because at higher than the optimal amounts, although the reaction rate is still increasing, the catalyst system is rapidly exhausted so that the reaction dies at a lower conversion. The data can be explained by assuming formation of free radicals by the induced decomposition of the peroxide either by the acetoin, the ferrous iron, or a complex between the iron and acetoin. This free radical then initiates polymerization. The acetoin free radical residue can induce the further decomposition of the peroxide or possibly can reduce ferric iron to ferrous. Other compounds yield similar results.

Introduction

Some of the earliest studies of activated polymerization reactions are those of Stewart (49,50,51,52,53) in which redox catalysts composed of a polymerization initiator, a heavy metal, and a phosphate or polyphosphate such as pyrophosphate or fructose diphosphate, an organic acid, or a polyhydroxy compound such as dextrose. E. I. du Pont de Nemours and Co. patented similar systems (44).

The German work developed the desirable combination of an oil soluble peroxy compound and a water soluble reducer in combination with a heavy metal carrier to a high degree. These results were summarized by Weidlein (63) who mentioned the system benzoyl peroxide - ferrous fatty acids - sorbose - sodium pyrophosphate. Later several publications appeared in Germany (17, 18,19,20,21,31,33) describing their earlier work and several in the United States describing the studies there which were stimulated by the earlier report (63).

Wall and Swoboda (62) attempted to formulate the reactions of such a system. Some credence to their postulate could be given when such highly

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insoluble peroxides as benzoyl peroxide were used and when the study of Marvel *et al.* (35) showed that a water soluble peroxide such as hydrogen peroxide disappeared from the medium prior to polymerization. However, the work published by Fordham and Williams (5,6,7,8,9), by Kharasch *et al.* (22,23) and by Kolthoff *et al.* (24,28,30) strongly suggested that the most probable locus of initial free radical formation was in the aqueous phase.

Sugars or similar materials have been used as reductant in reduction activation (31,44,49,50,51,54). The use of three parts of dextrose has been mentioned in many papers (32,39,47,58,59,61) and the use of about one part in many others (4,11,20,29,33,39,46,47,48,58,64). Sorbose (10,13,14, 19,20,62,63), dihydroxyacetone (20,26,27,30,33), ascorbic acid (31,33) invert sugar (60), lactose (60), fructose (25,60), and scylloinosose (30) have also been mentioned. Longer lists of materials tested were published (10,12, 18,29,36,37). These lists include many of the above compounds also. The use of amines, sugars, and ferrous iron mixed has been shown to be a versatile and effective system (4,48).

Studies of the role of enediols or alpha ketols in emulsion polymerization have been largely confined to comparisons between effective materials (4,12, 18,19,20,30,31,33,36,37,39,44,49,50,51,60). The general concept in these papers would appear to be that the sugar is a reductant whose prime purpose is to reduce the ferric iron to ferrous. The most extensive description of the reactions has been that of Kolthoff and Medalia (25,38). The mechanism suggested included induced decomposition of the peroxide by ferrous iron and by the sugar and also reaction of the free radicals produced by either process with the sugar to produce another radical. In subsequent publications the advantages of dihydroxyacetone (26) and ferrous sulphide (27) as reductants were indicated but significantly the differences in the relative effectiveness of sugars at 30° and 0°C. was discussed (29). Fryling *et al.* also compared a number of sugars (10) at 15°C. They concluded that an enediol equilibrium permitted the use of these materials in a low iron recipe. Kharasch *et al.* (23) concluded that ferric iron was not reduced by the sugar, that a free radical was formed by reaction of a free radical with the sugar, and that the sugar free radical reduced the ferric iron.

Generally speaking the concept which guided the present study was that the sugar was the reductant when complexed with iron. Further, an investigation of the role of enediols or alpha ketols in emulsion copolymerization might lead to a better understanding of the mechanism of redox with the aim of reducing or eliminating entirely the amount of ferrous iron or enediol added. This iron, if any remained in the polymer, was suspected to be the cause of degradation of the polymer (43) and the glucose caused fermentation of the latex and instability. The polyamines promised to be a replacement for the sugar and most of the iron so that the investigation of the role of the enediols was not carried beyond that stage where the mechanisms seemed at least plausible.

Experimental Techniques

Polymerizations were conducted in 8 oz. screw cap bottles, the caps of which were pierced and fitted with self sealing and oil resistant gaskets so that samples would be inserted or withdrawn by a syringe and needle. To the bottles was added the soap and electrolytes dissolved in most of the water and methanol (when used). Most of the styrene and all of the MTM was then added. The bottles were flushed of oxygen by adding more than the desired weight of butadiene and allowing the excess to evaporate, driving out the air. The bottles were securely capped when the correct weight was reached and inserted in a constant temperature bath where they were rotated end over end until cooled. The activator was then added and after a few minutes the catalyst in the rest of the styrene thereby starting the reaction. After the desired period of time the stopping agent was added and the degree of conversion determined by measuring the amount of rubber formed from the monomers. The stopping agent was a 7.5% dispersion of ditertiary butyl hydroquinone in the emulsifier used (15% solution). Investigations were carried out at 5°C. and -18°C. The recipes used are shown in Table I.

TABLE I
POLYMERIZATION RECIPES

	I	II
Monomers		
Butadiene	72 parts	70 parts
Styrene	28	30
Aqueous phase		
Water	180	157
Dresinate 214 (Hercules Powder Co.)	4.7	-
Potassium fatty acid soap flakes (Swift and Co.)	-	5.1
Daxad 11 (Dewey and Almy Chem. Co.)	0.10	0.10
Methanol (du Pont Synthetic)	-	46
KCl	0.25	-
K ₂ SO ₄	-	0.2
Modifier		
MTM (Phillips Petroleum Co.)	0.24	0.24
Activator		
FeSO ₄ /K ₄ P ₂ O ₇ ratio	1:1	-
FeSO ₄ /K ₄ P ₂ O ₇ /As ₂ O ₃	-	1:1:1
Catalyst		
CHP, cumene hydroperoxide (Hercules Powder Co.)	0.10	-
DIP, diisopropylbenzene monohydroperoxide (Hercules)	0.10	0.15
Polymerization temperature	+5°C.	-18°C.

The activator was made by mixing solutions of the ingredients and aging the resultant suspension 30 min. at 60°C. in a bottle with nitrogen atmosphere. The amount of activator was varied as indicated in each experiment, i.e. by the amount of ferrous sulphate used, the other ingredients remaining in equimolar ratio. Greater detail will be found in two earlier papers (41,42) and others from this laboratory (4, 39, 48).

The α -ketol under investigation was added by injection into the bottle. Most were water soluble and were added in aqueous solution the water being withheld from the initial charge. Benzoin, which was oil soluble, was added in styrene solution, the styrene being withheld from the initial charge.

Experimental Results

Acetoin in Polymerization Systems

The first step in the investigation was to investigate the effect of α -ketols using initiating systems of varying concentration. Acetoin, one of the simplest α -ketols, was chosen for this phase of the work. A typical example of what happened when acetoin was added to a system containing insufficient ferrous iron is shown in Table II.

TABLE II
EFFECT OF ACETOIN ON LOW IRON RECIPE* AT 5°C.

Acetoin (parts)	% Conversion at 17 hr.	
	(a)	(b)
0	16.9	4.5
0.2	32.0	21.1
0.4	43.2	36.5
0.6	47.0	—
0.8	52.6	47.5
1.0	48.9	46.9

* Recipe 1, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.10 part, cumene hydroperoxide 0.10 part.

Thus, for a 17 hr. reaction cycle the polymer yield had reached its maximum at 0.8 part acetoin. The results in column (a) were obtained using only experimental precautions already outlined. For column (b) all solutions were heated to 60°C. and nitrogen than bubbled through to remove oxygen dissolved in the various components of the recipe. It may be seen that the point at which the maximum was reached did not alter and for this reason the experimental precautions previously outlined for the removal of oxygen were considered sufficient. To make the reason for this maximum yield clearer, time-conversion studies were made at points below and above the optimal acetoin content with the results shown in Fig. 1. It may be seen that as the acetoin content increased, the initial rate increased but the conversion time relationship departs from linearity and after a given time no further reaction takes place. It is this effect, normally known as "dying," that causes the polymer yield to be less when larger amounts of reducers are used.

The optimal acetoin content was determined as a function of ferrous iron content, hydroperoxide content, and hydroperoxide type. The data thus determined are shown in Table III and Fig. 2.

It is obvious that the optimal acetoin content diminishes with increasing ferrous iron content and differs for different polymerization temperatures and hydroperoxide catalysts.

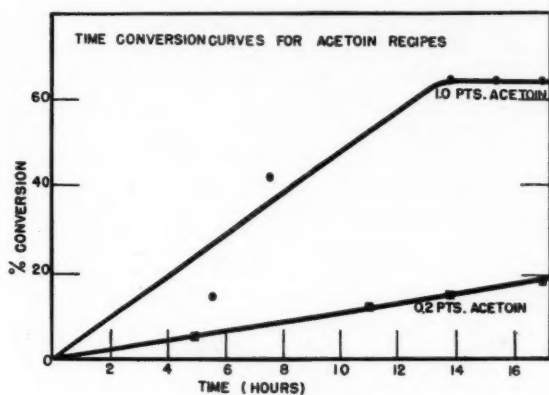


FIG. 1. Time conversion curves with acetoin in recipe.

 TABLE III
 OPTIMAL ACETOIN CONTENT RELATIONSHIPS

Temp., °C.	Ferrous iron content (part)	Optimal acetoin content (part)	Hydroperoxide content (part)	Hydroperoxide type
5	0.07	1.0	0.10	CHP
	0.10	0.8	0.10	"
	0.14	0.4	0.10	"
	0.18	0.0	0.10	"
	0.07	0.4	0.05	"
	0.06	0.4	0.10	DIP
	0.08	0.4	0.10	"
	0.16	0.0	0.10	"
-18	0.10	0.8	0.15	"
	0.15	0.0	0.15	"

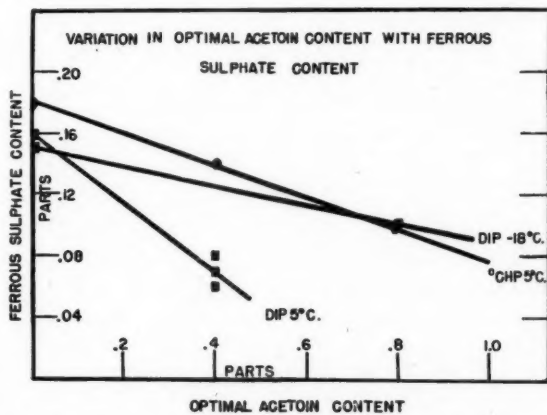


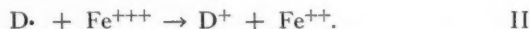
FIG. 2. Optimal acetoin concentration versus iron concentration in recipe.

Investigation of Various α -Ketols

An explanation of the role of α -ketols has recently been advanced (23) on studies made of solution polymerization. The α -ketol (DH) and the initiating free radical (RO) \cdot may undergo the following reaction:



Here D \cdot rather than DH represents the species effective in reducing as illustrated in the following equation.



Reasoning on this basis, the rate of reaction II will depend on the steady state concentration of D \cdot which in turn will be dependent on the absolute rate constant of reaction I. Thus, if acetoin and the RO \cdot generated from CHP react more slowly in I than acetoin and the RO \cdot generated from DIP, the steady state concentration of D \cdot must be much smaller when CHP is used as the hydroperoxide than when DIP is used. For this reason acetoin will tend to appear a much weaker reducing agent in the presence of CHP than it is with DIP.

The slope of the ferrous iron optimal acetoin content relationship may be adopted as a measure of the over-all efficiency of an α -ketol in emulsion polymerization. It represents the sum of two terms, one due to reaction I and the other due to reaction II. This quantity, which may be defined as the reduction coefficient, for various metal-hydroperoxide-ketol combinations may be tabulated. Various α -ketols were evaluated in the presence of CHP and 0.14 part $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Knowing this optimal α -ketol content at this ferrous iron content and assuming that the ferrous iron content at or above which α -ketols at all concentrations lowered the polymer yield was constant, it was possible to calculate the slope of the corresponding ferrous iron optimal α -ketol content relationship. In Table IV are compiled the slopes which were determined for various α -ketols under various conditions.

TABLE IV

A SUMMARY OF REDUCTION COEFFICIENTS

α -Ketol	Hydroperoxide	Temp., $^{\circ}\text{C}$.	Reduction coefficient (moles Fe^{++} /mole α -ketol)
Acetoin	DIP	5	0.070
Acetoin	CHP	5	0.024
Acetoin	DIP	-18	0.006
Tartaric acid	CHP	5	0.017
Lactic acid	CHP	5	0.001
Gluconic acid	CHP	5	0.050
Benzoin	CHP	5	0.040
Arabinose	CHP	5	0.027
Galactose	CHP	5	0.035
Sorbose	CHP	5	0.036
Dextrose	CHP	5	0.035

As was pointed out, the reduction coefficient of acetoin increased markedly upon changing from CHP to DIP. Also of interest is the large decrease of the reduction coefficient with decreasing temperature. This would seem to restrict the usefulness of α -ketols in subzero polymerizations. As a change from one α -ketol to another is made, the reduction coefficient undergoes changes of a fairly large magnitude. Sugars containing six carbon atoms, such as dextrose, sorbose, and galactose show the same reducing effects regardless of their internal configuration. Arabinose, possessing only five carbon atoms, shows distinctly lower reduction coefficient. This may be attributed to the extra hydroxyl groups and is supported by the experience with hydroxy acids in which the reduction coefficient steadily rises from a low with lactic acid through tartaric acid with gluconic acid representing the most promising reducer tested. An oil soluble α -ketol benzoin, showed surprisingly good results considering that all reaction must take place either along an oil water interface or in the soap micelles.

Rates of Polymerization with Various α -Ketols

It was observed that somewhat different yields were obtained using the various α -ketols. A summary of the results is shown in Table V. The results shown are the optimal for the various experiments.

TABLE V
OPTIMAL CONVERSION FOR VARIOUS CONCENTRATIONS OF α -KETOL

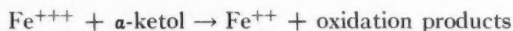
α -Ketol	Moles $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ / 100 gm. monomer $\times 10^4$	Moles α -ketol/100 gm. monomer $\times 10^3$	% Conversion (17 hr.)
Acetoin	2.5	11.4	46.6
Acetoin	3.6	9.1	52.6
Acetoin	5.0	4.6	74.1
Acetoin	6.1	0	91.1
Tartaric acid	5.0	6.6	70.8
Lactic acid	4.0	41.0	41.7
Gluconic acid	5.0	2.0	47.5
Benzoin	5.0	2.8	31.3
Arabinose	5.0	4.0	76.2
Galactose	5.0	3.3	69.9
Sorbose	5.0	3.1	73.2
Dextrose	5.0	3.3	80.0

Thus it is evident that as the iron content is decreased with a corresponding increase in the α -ketol content, the conversion is lowered. This may be due to the greater concentration of $\text{D} \cdot$ free radicals which act as retarders of polymerization through combination with other free radicals. Some of the hydroxy acids are the most active in this respect although tartaric acid seems to be an exception. Sugars, in general, yield quite rapid rates of conversion. Acetoin is intermediate in this respect. Benzoin seems to be a strong retarder possibly because all free radicals produced from benzoin are near the locus of initiation of the polymerization reaction and receive ample opportunity for recombina-

ation with the growing polymer chain. It may be that the tendency of the different α -ketols to complex with ferrous iron have a decided effect on the polymer yield. This type of reaction has been observed (3) but as yet no study of its contribution to the polymerization in emulsion has been made.

Discussion

On plotting of the data in Table III it is evident that there is a linear relationship between the initial ferrous iron content and the amount of acetoin necessary to bring about a maximum in the polymer yield (Fig. 2). The slope of this relationship should be dependent on the relative ease of the reaction



i.e. where the α -ketol used is a powerful reducing agent, only a small amount of α -ketol would be necessary to compensate for a relatively large reduction in the initial ferrous iron content. Hence a greater slope will be shown in this α -ketol ferrous iron relationship for stronger reducing agent than for weaker reducing agents. This, however, does not describe the experimental data, for when DIP was substituted for CHP, the slope increased markedly, indicating that it was not alone dependent on the α -ketol type. Indeed this observation appears to invalidate the explanation of the role of reducers in redox polymerization, i.e. as reducers of ferric iron. Rather the iron-sugar complex is the primary reducer and the sugar free radical may reduce ferric ion to ferrous subsequently and incidentally.

That sugars may form a complex with iron has been indicated by several publications (3,4,25,55,56,57). On the other hand the digestion (10) of dextrose may result in many compounds such as fructose, acids, and oxidation products (12). Any of the products may be capable of forming complexes with iron which may in fact behave like antioxidants through the mechanism postulated by Kolthoff (25) and formulated by Kharasch (23). For instance sugars retard the autoxidation of ascorbic acid (15,16) whereas iron catalyzes the autoxidation.

The work of Embree *et al.* (4) strongly suggests that sugars are also able to form complexes with amines which complexes are still powerful reductants in the virtual absence of iron but are not destroyed by cyanoethylation reaction with acrylonitrile (4,64). That amines and sugars may form complexes has been indicated (34,40,45).

In the iron-hydroperoxide catalyst activator systems the sugar or other α -ketol, combined in complex form with iron, acts as the reductant for part or all of the induced decomposition of the cumene hydroperoxide. It seems likely that ferric complexes with sugar are formed readily and are active reducers. When ferrous iron is used there is the additional possibility of active reduction of the hydroperoxide by the ferrous iron. The reductant such as acetoin, dextrose, etc., has a ferrous iron sparing action.

The other mechanism is to complex polyamines in such a manner that the complex is still an active reductant for cumene hydroperoxide but is not susceptible to the destruction by the cyanoethylation reaction when acrylonitrile is present. Thus the amine-sugar combinations form very effective activators even for butadiene-acrylonitrile copolymerization reactions. The nature of this complex is not readily understood. An alternative explanation, namely, that the polyamine can replace the ferrous iron in the sugar complex does not seem quite as probable since iron has amazing specificity of action. However, slow dissociation of the amine sugar complex to yield the free amine is possible.

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THE PAPILIONACEOUS ALKALOIDS

XIV. CONCERNING SPATHULATINE AND NONALUPINE¹

BY LÉO MARION

Abstract

The two alkaloids nonalupine and spathulatine reported in the literature have been found to be identical and to consist of the monohydrochloride of pusilline, $C_{15}H_{23}N_2$. On heating *in vacuo* the hydrochloride undergoes disproportionation, giving rise to the free base and the dihydrochloride. The peculiar reactions of spathulatine are explained by the fact that they simply liberated the base from its salt. Pusilline forms a dipicrate containing an additional mole of picric acid, which accounts for the necessity of using a solution of that acid for its recrystallization.

Spathulatine was first described by Couch (1) who found it in a plant first thought to be *Lupinus spathulatus* Rydb., but the identification of the species was subsequently questioned and the plant assumed to have been *L. marianus* Rydb. (2). Later, in an investigation of *L. sericeus* Pursh, the same author again reported the presence of spathulatine and a new, neutral alkaloid that he designated nonalupine (2). The latter has also been found by Couch in *L. andersonii* Wats. (3). Both alkaloids have high melting points and have been assigned widely different empirical formulae, i.e., $C_{33}H_{64}O_6N_4$ (spathulatine) and $C_{15}H_{24}ON_2$ (nonalupine). The empirical formula of spathulatine, unusual in the papilionaceous alkaloids, and the anomalous neutrality of nonalupine, which according to its assigned formula contains two nitrogen atoms and only one oxygen, rendered a further study of these bases interesting. Such an investigation was undertaken with quantities of material kindly provided by Dr. James F. Couch.

Nonalupine has been described as forming a hydrate, $C_{15}H_{24}ON_2 \cdot 2H_2O$, melting at 91.5–92.5°, which after drying at 110° softened at 219° and melted at 235° (2). The sample of nonalupine received from Dr. Couch melted at 87–90°. In order to purify it, it was distilled *in vacuo*, but was found under those conditions to be fractionated into a low-boiling oil and a solid subliming at a higher temperature. The oil gave rise to a crystalline monoperchlorate identical with the monoperchlorate of pusilline (4). Nonalupine picrate when recrystallized from methanol containing picric acid melted at 183.5–185.5°. Although it had not been possible earlier (4) to prepare a crystalline picrate from pusilline by using the calculated quantity of picric acid, this has now been done successfully by employing an excess of picric acid. Pusilline picrate proved to be identical with nonalupine picrate. This fact and an examination of the reported analytical figures of nonalupine suggested that this alkaloid might not be a base but a base hydrochloride, which would account for its high

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melting point. Indeed, this has been found to be so, and the sublimate described above has been shown to be the dihydrochloride of pusilline, identical with the salt prepared by neutralizing pusilline with hydrochloric acid.

Since pusilline is an oil and its dihydrochloride a high melting solid, nonalupine which is a crystalline substance cannot be a simple mixture of the two. Nonalupine, without previous distillation, was therefore recrystallized from acetone. It consisted of a beautifully crystalline solid that proved to be pusilline monohydrochloride monohydrate, identical with a specimen prepared by titrating pusilline with methanolic hydrochloric acid to a phenolphthalein end point. Hence, nonalupine is not a base but pusilline monohydrochloride, and it is noteworthy that this salt on heating *in vacuo* undergoes disproportionation giving rise to pusilline and its dihydrochloride.

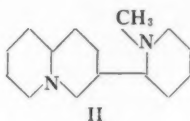
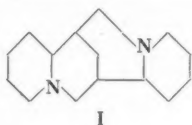
The recorded melting point of the picrate of spathulatine was almost the same as that of nonalupine and when recrystallized both salts were found to be identical. Therefore, spathulatine picrate is pusilline picrate. A comparison of the reported analytical figures of spathulatine with those of nonalupine (2) shows that the nitrogen content is about the same. Furthermore, the melting points of the two compounds are the same (spathulatine, m.p. 233–234° and nonalupine, m.p. 235°). Unfortunately, Dr. Couch's samples do not include one of spathulatine itself so that a direct comparison cannot be made, but it is highly probable that the substance is identical with nonalupine and hence that it consists of pusilline monohydrochloride monohydrate.

Spathulatine is said to be decomposed by boiling hydrochloric acid to an isomer of spartyrine isolated as its perchlorate (2). The recorded melting point of this perchlorate is the same as that of pusilline perchlorate (4) and the reported analytical figures are in good agreement with those required for this salt. It seems obvious that no reaction took place and that in the process of isolation of the product the base was simply liberated from its hydrochloride and converted to its perchlorate.

There remained to explain the peculiar potassium iodide addition complex of spathulatine. Couch's specimen of this compound was recrystallized several times from boiling acetone and thus separated from what proved to be an excess of potassium iodide. The final crystalline product that separated from the acetone solution consisted of pusilline monohydriodide. This salt has been shown to be the product of an ionic interchange between pusilline monohydrochloride and potassium iodide and to be identical with the hydriodide prepared by titrating pusilline with hydriodic acid. The identity of the so-called complex with pusilline monohydriodide as well as its method of formation supplies the proof that spathulatine is pusilline monohydrochloride and that it is, therefore, identical with nonalupine. Consequently both the names spathulatine and nonalupine should be deleted from the literature.

The close similarity between the properties of pusilline and those of sparteine was pointed out earlier (4). Although the analytical figures obtained with

the base and its various salts are not all in complete agreement with theory, the best empirical formula derivable from these is $C_{15}H_{28}N_2$. No double bond appears to be present since pusilline in dilute hydrochloric acid solution does not absorb any hydrogen in the presence of Adams' catalyst, and this seems to confirm the assigned hydrogen content. Further, since pusilline contains one N-methyl group (4) and its infrared absorption spectrum does not reveal the presence of any NH group, it must contain one ring less than sparteine (I) and its most probable structure appears to be II.



Experimental²

Nonalupine

The sample supplied by Dr. Couch was a light brown crystalline substance, m.p. 87–90°. When a portion (1.00 gm.) was distilled *in vacuo*, two fractions were obtained: an oil, b.p. 140–145°/0.12 mm., wt. 0.35 gm., and a white solid that sublimed at 160–180°/0.12 mm., wt. 0.63 gm. The oily fraction when redistilled boiled at 95–100°/0.2 mm., and consisted of a colorless liquid. It was dissolved in methanol and the solution made just acid to Congo red with 65% perchloric acid. A crystalline perchlorate that separated after a few drops of acid had been added had all dissolved when the neutral point was reached. Addition of ether brought down an amorphous perchlorate that could not be induced to crystallize. On the assumption that the amorphous salt was a diperchlorate while the crystalline salt that had first separated was a mono-perchlorate, the ether was evaporated and two drops of ammonium hydroxide were added to the residual solution. A crystalline salt separated immediately which was recrystallized from methanol. It consisted of long flat needles, m.p. 217°. In admixture with pusilline perchlorate (4) the melting point was unchanged. Calcd for $C_{15}H_{28}N_2 \cdot HClO_4$: C, 53.49; H, 8.62%. Found: C, 53.63; H, 8.78%.

Some of the base recovered from the perchlorate was distilled *in vacuo* and analyzed. Calcd for $C_{15}H_{28}N_2$: C, 76.20; H, 11.94; N, 11.85%. Found: C, 76.71, 76.60; H, 10.62, 10.81; N, 12.04, 12.35%.

The solid fraction that sublimed at 160–180°/0.12 mm. (see above) was recrystallized twice from boiling ethyl acetate from which it separated as closely packed clusters of fine needles. It began to sinter at 262° and melted at 270–273°. An aqueous solution of a small quantity of the substance containing a drop of nitric acid produced a white precipitate on the addition of a little silver nitrate. It was dried *in vacuo* at 100° prior to analysis. Calcd for $C_{15}H_{28}N_2 \cdot 2HCl$: C, 58.24; H, 9.78; N, 9.06; Cl, 22.92%. Found: C, 58.01;

²All melting points are corrected.

H, 9.53; N, 9.30, 9.44; Cl, 22.10, 21.66%. This salt was difficult to crystallize and separated only on long standing. The analytical results indicate that it was not quite pure.

This dihydrochloride was dissolved in methanol and added to a methanolic solution of picric acid. A lemon-yellow picrate separated which was recrystallized from a methanolic solution of picric acid.³ It separated as clusters of small yellow prismatic needles, m.p. 183.5–185.5°. A sample of Couch's nonalupine picrate after recrystallization from a methanolic solution of picric acid melted at 183.5–185.5° either alone or in admixture with the above picrate.

A small quantity of freshly distilled pusilline was dissolved in methanol and the solution made just acid to Congo red by the addition of methanolic hydrochloric acid. The resulting solution was evaporated to dryness, the residue redissolved in methanol and again evaporated. The residue was dissolved in boiling ethyl acetate from which the salt crystallized slowly on standing as small warts. It began to sinter at 260° and melted at 269–271° either alone or in admixture with the sublimate above.

Pusilline Picrate

A small sample of pusilline (4) was dissolved in methanol and added to a solution of an excess of picric acid in methanol. A picrate separated which after recrystallization from a solution of picric acid in methanol, consisted of clusters of pale yellow prismatic needles, m.p. 183.5–185.5°, either alone or in admixture with nonalupine picrate. Calcd for $C_{15}H_{23}N_2 \cdot 3C_6H_3O_7N_3$: C, 42.91; H, 4.04; N, 16.68%. Found: C, 42.89, 42.66; N, 3.54, 3.50; N, 16.52%. The analysis shows that an additional mole of picric acid is present over that required for a dipicrate, which accounts for the necessity of an excess of picric acid to bring about crystallization.

Pusilline Monohydrochloride

In order to determine the nature of nonalupine itself, a quantity was recrystallized without previous distillation. It was dissolved in acetone, the solution boiled with a little charcoal and filtered. The filtrate when concentrated and cooled deposited beautiful colorless prismatic needles which melted at 88–90°, resolidified, began to fuse at 220° and melted at 235.5–236.5°. The melting point of nonalupine is given as 235° after softening at 219°. Calcd for $C_{15}H_{23}N_2 \cdot HCl \cdot H_2O$: C, 61.93; H, 10.74; N, 9.63%. Found: C, 62.27, 62.41; H, 10.11, 9.98; N, 9.41, 9.56%.

A quantity of freshly distilled pusilline was dissolved in methanol and titrated with methanolic hydrochloric acid to a phenolphthalein end point. The solution was evaporated to dryness on the steam bath, the residue dissolved in methanol and the resulting solution again evaporated to dryness. The crystalline residue was dissolved in boiling acetone from which the salt separated as colorless prismatic needles. Like "nonalupine" it melted at 88–

³This picrate does not recrystallize from pure methanol and requires the presence of excess picric acid to form crystals.

90°, resolidified and melted again at 235.5–236.5° after beginning to fuse at 220°. Mixture of the two did not alter these constants.

Pusilline Monohydriodide

A sample of spathulatine – potassium iodide compound obtained from Dr. Couch was boiled with acetone. A portion did not dissolve and was filtered off. The insoluble material proved to be potassium iodide. The filtrate was concentrated to a small volume and allowed to cool. Colorless prismatic needles separated that melted at 252.5° after sintering at 250.5°. Calcd for $C_{15}H_{23}N_2$. HI: C, 49.44; H, 8.02; N, 7.69%. Found: C, 49.62; H, 7.79; N, 7.62%.

Pusilline monohydrochloride was dissolved in methanol and added to a solution of potassium iodide in methanol. After boiling for five minutes the solution was evaporated to dryness and the residue boiled with acetone. The mixture was filtered hot to remove the insoluble excess potassium iodide and the filtrate evaporated to dryness. The residue was again boiled with acetone, the solution filtered and concentrated on the steam bath. On cooling it deposited colorless prismatic needles, m.p. 252.5°, either alone or in admixture with Couch's recrystallized "spathulatine – potassium iodide compound."

Pusilline hydriodide was also prepared by titration of a methanolic solution of pusilline with methanolic hydriodic acid to a phenolphthalein end point. The salt, after recrystallization from acetone, melted at 252.5°, either alone or in admixture with the salt prepared by the action of potassium iodide on pusilline monohydrochloride.

Furthermore, a quantity of "spathulatine – potassium iodide complex" was decomposed with aqueous potassium hydroxide and the recovered base converted to the monoperchlorate, m.p. 217° either before or after mixture with pusilline monoperchlorate.

Spathulatine Picrate

A quantity of this salt supplied by Dr. Couch was recrystallized twice from a methanolic solution of picric acid. It was obtained as small clusters of lemon-yellow prismatic needles, m.p. 183.5–185.5°. Mixing with pusilline picrate or nonalupine picrate failed to depress the melting point. Calcd for $C_{15}H_{23}N_2 \cdot 3C_6H_3O_7N_3$: C, 42.91; H, 4.04%; Found: C, 43.12; H, 3.81%.

Acknowledgment

The author wishes to express his gratitude to Dr. James F. Couch, Eastern Regional Laboratory, United States Department of Agriculture, Philadelphia, Penn., for his most generous gift of these alkaloids and their salts.

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THE BIOGENESIS OF ALKALOIDS

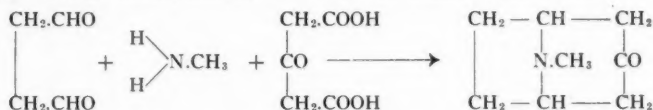
III. A STUDY OF HYOSCYAMINE BIOSYNTHESIS USING ISOTOPIC PUTRESCINE¹BY D. G. M. DIAPER,² SAM KIRKWOOD,³ AND LÉO MARION

Abstract

Putrescine-1: 4-C¹⁴ was fed to mature *Datura stramonium* in an investigation of the biosynthesis of *l*-hyoscyamine. Although C¹⁴ was metabolized by the plant, no radioactivity was found in the isolated alkaloid; the mechanism of biosynthesis of the tropane nucleus is discussed in the light of published work and of this observation.

Introduction

A theory of biogenesis of the tropane nucleus from ornithine was first developed by Robinson (18, 19) after an *in vitro* synthesis of tropinone from succindialdehyde, methylamine, and acetone-dicarboxylic acid.



Degradation of arginine, proline, and ornithine to succindialdehyde or γ -aminobutyraldehyde and its related carbinolamine are plausible intermediate steps in the synthesis of the tropane system. Another plausible intermediate is putrescine, 1: 4-diaminobutane, also closely related to this group of amino acids.

Cromwell (6, 7) has collected evidence that points to putrescine acting as a precursor of *l*-hyoscyamine in *Atropa belladonna* and *Datura stramonium*. Minor increases in percentage of alkaloid in stem and leaf were reported following injection of putrescine through stem stumps. Additional evidence was demonstration of the presence of a diamine oxidase (capable of converting putrescine to succindialdehyde) and of small amounts of putrescine in *A. belladonna*.

James (11), working with detached leaves and using statistical methods of evaluation, considers that significant increase in yield of *l*-hyoscyamine followed feeding of ornithine or arginine to *A. belladonna*. He has failed to demonstrate enzymic degradation of ornithine to putrescine by tissue preparations of *A. belladonna* (12) but has prepared a polyphenolase from this plant that causes oxidation of ornithine to α -keto- δ -aminovaleric acid (13).

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It seems most probable, therefore, that the ornithine-arginine system of amino acids acts as a precursor of the tropane alkaloids. There is, however, conflicting evidence for each of two possible metabolic routes from amino acid to alkaloid.

In the present work, the role of putrescine in biosynthesis of hyoscyamine in *D. stramonium* has been investigated by a tracer technique. Putrescine-1:4- C^{14} was synthesized by standard methods and administered to mature *D. stramonium*; the alkaloid was isolated by a carrier technique.

Experimental

Putrescine-1:4- C^{14}

Several synthetic routes to putrescine were explored with a view to selection of that most easily employable in microsynthesis with compounds containing C^{14} . One unsatisfactory route was based upon reduction of γ -phthalimidobutyronitrile (15) which, in our hands, gave poor yields of putrescine upon reduction with sodium and ethanol. When the nitrile (1.02 gm.) in ethanol (3 cc.) in the presence of ammonia (1.0 cc., sp. gr., 0.88) was hydrogenated at 1500 lb. and 100° over Raney nickel, a 91% yield of putrescine was obtained; phthalimide was the other major product. This route was abandoned because synthesis of γ -phthalimidobutyronitrile containing C^{14} would involve separation of small quantities of liquid intermediates (2).

The route adopted involved hydrogenation of succinonitrile; the latter being obtained from potassium cyanide- C^{14} by a method similar to that of Kushner and Weinhouse (16). Potassium cyanide- C^{14} was made from barium carbonate- C^{14} by fusion with sodium azide (1). Difficulties encountered by us in this preparation were similar to those already reported (10) but unexpected difficulty was encountered in evaporating to dryness aqueous solutions containing potassium cyanide. To avoid loss of cyanide by alkaline hydrolysis and by volatilization of hydrogen cyanide, it was necessary to neutralize excess of potassium hydroxide with (nonradioactive) hydrogen cyanide, basify with ammonia, and concentrate *in vacuo* over calcium chloride. Presence of the anion of a mineral acid in the ammoniacal solution reduced the pH (by buffering) and considerable loss of cyanide was experienced.

To a residue of potassium cyanide- C^{14} (obtained from 1.288 mgm. of barium carbonate at a radioactive level of 4.2×10^7 counts per minute) were added 0.615 gm. of potassium cyanide, a trace of potassium iodide (9), 1.0 cc. of water and 3.0 cc. of ethanol. Ethylene dibromide (1.61 gm., 1.18 equiv.) was added and the mixture was boiled, under reflux, for 75 min. After addition of water (100 cc.) and removal of unchanged ethylene dibromide with the aid of ether, the mixture was treated with sulphuric acid (5 N, 20 cc.) and, after 30 min. at room temperature to hydrolyze isocyanides, succinonitrile was isolated by continuous extraction with chloroform. Evaporation of the extract gave a crystalline residue (222 mgm.) of succinonitrile which was not further purified.

A solution of succinonitrile- C^{14} (222 mgm.) in ethanol (2 cc.) containing Raney nickel was cooled and an equal volume of liquid ammonia was added. The vessel was quickly sealed in a bomb and hydrogenation of the nitrile was performed at 100° and 1200 p.s.i. (4). The reaction mixture was added to 500 cc. of dilute hydrochloric acid and, after filtration, putrescine-1:4- C^{14} was precipitated as the *reineckate* (362 mgm., at a radioactive level of 3.8×10^6 counts per minute.) Calc. for $C_{12}H_{30}O_2N_{14}S_8Cr_2$: N, 25.7%. Found: N, 26.0%. It was found that the *reineckate* is a useful solid derivative of this base. It is quantitatively precipitated from aqueous solution by ammonium *reineckate* and this gravimetric estimation method is unaffected by ammonium chloride at 60 gm. per liter. Putrescine can thus be sharply separated from ammonia. The *reineckate* is soluble in acetone. Recovery of putrescine from this derivative was accomplished by the method of Kapfhammer and Bischoff (14) or more conveniently by heating with strong potassium hydroxide solution and trapping the vapors in hydrochloric acid.

Cultivation of Datura stramonium and Feeding Experiments

Seeds of *D. stramonium* were sown in boxes in a greenhouse at the beginning of October. In mid-December the seedlings were transferred to beakers of a hydroponic nutrient solution and feeding experiments with putrescine hydrochloride were performed on the mature plants in the following April, May, and June. The nutrient solution employed contained potassium nitrate, 500 mgm. per liter; calcium nitrate, 1180 mgm. per liter; magnesium sulphate, 495 mgm. per liter; potassium dihydrogen phosphate, 136 mgm. per liter; ferric tartrate, 48 mgm. per liter; and traces of micronutrients (Mn, B, Cu, Zn). Light was excluded from the beakers of solution to minimize growth of algae on the roots.

Four feeding experiments were performed, each in total darkness to eliminate photosynthesis and consequent randomization of C^{14} in the alkaloid (8). In two of the experiments the putrescine hydrochloride was administered, in dilute solution in distilled water, through the roots; in the other two experiments the solution was administered to the wilted plant by uptake through a cut stem. A single healthy plant with flower buds was used for each feeding experiment.

Isolation of Alkaloid

To establish the presence of *l*-hyoscyamine in the plants the alkaloid was isolated as follows: Aerial parts of two plants were oven-dried at 110° and powdered (24 gm.). Following continuous extraction with methanol and evaporation of the extract, the gummy residue was shaken with sulphuric acid (0.5 *N*, 200 ml., in three portions). Extraction with a mixture of chloroform (20 cc.) and ether (80 cc.) was used to free this aqueous extract from suspended gum and the basic material was liberated by ammonia. After extraction with three portions (totalling 300 ml.) of a similar chloroform-ether mixture, the extract was dried and evaporated, finally using suction at 100° . To the residue

of crude alkaloid (25 mgm.) was added dilute hydrochloric acid and 40 mgm. of gold chloride. A black oil separated. Extraction of this black oil with boiling water gave two crops of dark yellow crystals, totalling 16.5 mgm. Recrystallization afforded yellow plates, m.p., 160.5-161.5° undepressed in admixture with authentic hyoscyamine aurichloride. Isolation of the alkaloid as aurichloride (17) was found preferable to isolation as picrate (6) as the latter compound could be obtained only in a poor yield and crude state.

After a feeding experiment, the root, which contains hyoscyne (3) and aerial parts were extracted separately. Hyoscyamine (60-200 mgm.) as carrier was added to each extract. Isolation of the alkaloid was performed along the lines above, but samples of each fraction were counted in a "Nucleometer".

Samples were evaporated on aluminum dishes and counted as layers of finite thickness. Self-absorption corrections were applied, but reproducibility of counts was no better than 30%. Alkaloid aurichloride samples were recrystallized before counting as an infinitely thick layer.

Results

For location of radioactivity in treated plants, see Table I in which all figures represent total activity in the fraction described.

TABLE I
LOCATION OF RADIOACTIVITY

Experiment	Radioactivity administered (counts per min.)	Duration	Portion studied	Radioactivity found (counts per min.)			
				Residue (chiefly cellulose)	Fatty material	Water-soluble nonbasic material	Alkaloid aurichloride
1*	71,000	1 week	Root Shoots	3650 None	90 None	6450 300	None None
2*	530,000	41 hr.	Root Shoots	10,300 None	2200 110	72,000 1500	12 None
3†	100,000	24 hr.	Root Shoots	1100 4300	400 1810	790 21,000	20 None
4†	100,000	9 days	Root Shoots	None 2090	110 350	380 8000	None 10

* Uptake through the root.

† Uptake through the stem.

Uptake of C¹⁴ was followed from day to day in Experiment I, showing that selective disappearance of radioactivity from the solution was occurring. Concentrations of radioactivity in the solution in the first three days were 650, 320, and 140 counts per ml.

Recovery of C¹⁴ not absorbed was 960 counts per minute in Experiment 1; 100,000 in 2; 48,000 in 3; and 13,000 in 4.

The possibility of "water-soluble nonbasic material" containing C^{14} as putrescine was investigated by taking this stem extract from Experiment 3, basifying with sodium hydroxide, and extracting with ether. The ratio of C^{14} in the ethereal and aqueous solutions was 1:1.4.

Discussion

C^{14} detected in the *l*-hyoscyamine isolated was negligible in comparison with the amount of C^{14} administered. Those counts observed were probably due to impurity. These experiments do not lend support to the postulate of Cromwell (7) that putrescine is an intermediate in the biosynthesis of *l*-hyoscyamine in *D. stramonium*. On the other hand, positive evidence, in an investigation of this nature, is far more valuable than negative evidence.

If these experiments be interpreted to dismiss all consideration of putrescine as a precursor of *l*-hyoscyamine, and if the diamine oxidase of Cromwell (7) be accepted, there is doubt whether synthesis of the tropane skeleton from succinaldehyde occurs. To this must be added the fact that Cromwell was unable to demonstrate the presence of methylamine in *A. belladonna* or *D. stramonium*. On the other hand, the Robinson tropinone synthesis (20) and the demonstration by Schöpf and Lehmann (21) that it proceeds best at physiological pH are highly suggestive. Feeding experiments with labelled succinaldehyde and methylamine would be useful.

The present experiments are irrelevant to the possible route of *l*-hyoscyamine biosynthesis from ornithine through α -keto- δ -aminovaleric acid (12).

If an authentic tracer-containing intermediate in hyoscyamine synthesis were fed to a virile plant, it is reasonable to assume that the absolute amount of tracer in the alkaloid would rise quickly to a maximum and then decrease asymptotically to zero. We have no means of knowing the time-scale of this hypothetical curve, but the spread of experiment duration (24 hr. to 9 days) means that, if the putrescine hypothesis is to be retained, alkaloid turnover must be either very fast or very slow. It may be mentioned that *D. stramonium* does not survive in darkness for much more than a week.

It is difficult to know whether the conditions of the experiments (darkness, withdrawal of supplies of salts, administration of unusual ions) could sufficiently disturb the metabolism to arrest alkaloid synthesis. This is considered, however, to be unlikely.

The fate of C^{14} in the plants was consistently extensive incorporation into both methanol-soluble and methanol-insoluble fractions. Although purification of fats and cellulose was not attempted, it seems likely that both contained C^{14} . Much of the radioactivity appeared in the water-soluble nonbasic fraction; this contains sugars. It is possible to visualize a metabolic route for putrescine that leads through succinate into the tricarboxylic acid cycle and thence to carbohydrate and lipid synthesis (5).

The question of the presence of unchanged putrescine in the water-soluble nonbasic fraction must be left open. It is a stronger base than ammonia and would not appear in the alkaloid fraction; on the other hand, the value of the experiment using sodium hydroxide and ether cannot be assessed without knowledge of the amount of putrescine present and its partition coefficient. In any case, under the conditions of administration of a solution through a cut stem, some material must inevitably adhere to the surface without entering the plant vascular system at all.

Selective removal of C^{14} from the solution during root uptake experiments can be explained by metabolism of putrescine by the bacteria and algae unavoidably present on the roots. It is, however, considered likely that the radioactivity in the plant was derived from putrescine itself, rather than from uptake of any metabolites produced by microorganisms from the base. This objection is inapplicable to stem-feeding experiments.

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HYDROLYSIS AND POLYMERIZATION OF CYCLIC DIMETHYLETHYLENE OXALATES¹

BY L. G. RIPLEY AND R. W. WATSON

Abstract

Macrocrystalline cyclic oxalates (2,3-dimethyl-5-6-*p*-dioxanediones) were prepared by vacuum distillation of the polymeric mixture formed on heating ethyl oxalate, and 1,2-dimethylethylene glycol with an ester-interchange catalyst. Monomeric dimethylethylene oxalate polymerizes less readily than propylene oxalate, and only at an elevated temperature in the presence of a catalyst. Dimethyl substitution therefore confers marked stability on the six-membered ring. Hydrolysis reaches 50% completion almost instantaneously, followed by a slow first order reaction resulting in complete cleavage of the monobasic acid in about one month at room temperature. Hydrolysis constants for the *levo*- and *meso*-oxalates are 0.069 and 0.076 days⁻¹ respectively. The crystalline monomers do not possess sharp melting points and represent stereoisomeric mixtures which display optical activity in solution.

Reversible polymerization is a well known characteristic of six-membered cyclic esters (1). The unsubstituted esters, e.g. δ -valerolactone (6), the lactone of hydroxyethylglycolic acid (7), and ethylene oxalate (1) polymerize spontaneously at room temperature. As a general rule the presence of substituent groups markedly affects ring stability. The substituted six-membered esters, e.g. the lactone of 2,3,4-trimethyl-*l*-arabonic acid (5), propylene oxalate (1), and α -*n*-propyl- δ -valerolactone (2) require either heat or catalysts or both to effect polymerization. Carothers *et al.* (2) have noted that ease of polymerization is related to susceptibility to hydrolysis. The present investigation explores the relation between hydrolysis and polymerization in the previously uninvestigated dimethylethylene oxalates.

Immediate titration with 0.01 *N* sodium hydroxide of aliquots of freshly prepared aqueous solutions of the *levo*- and *meso*-oxalates showed 50-52% of the calculated total acidity. It appears therefore that 50% of the linkages in the dimethyl-substituted monomers are readily hydrolyzed. This anomaly may be explained by assuming rapid ring opening, followed by slow hydrolysis of the hydroxy acid. As shown in Fig. 1 hydrolytic cleavage of the monobasic acid is complete in about one month at room temperature. Hydrolysis constants of the *levo*- and *meso*-oxalates in this slow latter phase, determined from aliquots of aqueous solutions (see experimental section), were 0.069 and 0.076 days⁻¹ respectively.

Both dimethylethylene oxalates polymerize less rapidly than propylene oxalate (1). Repeated vacuum sublimation of the pure dimethyl monomers at temperatures just below their melting ranges failed to effect any apparent change in properties. Both the *levo*- and *meso*-monomers remained unchanged after storage under anhydrous conditions for more than one year. However,

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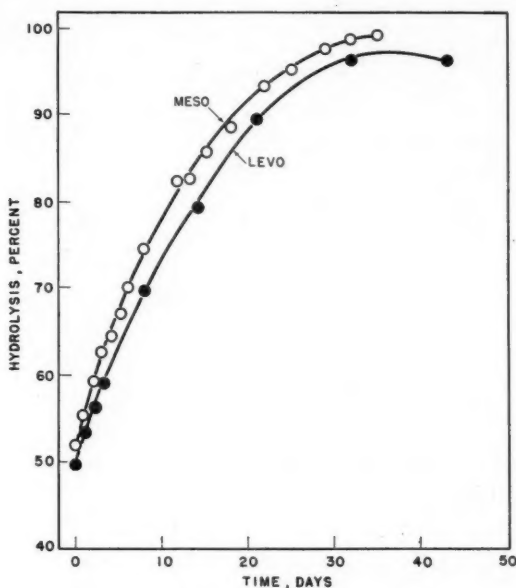


FIG. 1. Hydrolysis of *meso*- and *levo*-oxalates.

when either was heated with a trace of potassium carbonate at 110°C. under deoxygenated nitrogen, amorphous polyesters were formed in about one day. The highest polymer obtained under these conditions from the *meso*-oxalate was a hard resin, while the corresponding product from the *levo*-monomer was a viscous balsam. The inherent viscosities (4) in 2% acetone solution of these polymers are plotted against time of formation in Fig. 2. The reaction forming the *meso*-polyester is more rapid, and assuming an average value for K_{eqv} . (10, 11, 13) the molecular weight indicates the formation of an ω -polyester. During polymerization there is a loss in weight of less than 2%.

The comparison between ease of polymerization and hydrolysis in the oxalate series is shown in Table I. The fundamental observation (2) that ease of polymerization is related to susceptibility to hydrolysis may be explained by assuming that traces of water initiate polymerization. More rarely two six-membered rings may coalesce (3) but ordinarily the first step in chain formation is assumed to be hydrolytic ring opening to form the hydroxy acid. The hydroxyl group of the acid may then react with another ring to form the linear dimer (2).

The depression in the rate of polymerization of cyclic oxalates with increasing methyl substitution may be explained through the comparatively low reactivity of secondary hydroxyl groups. Adjacent methyl groups introduce steric effects as well as changes in bond strength. In the compounds under investigation,

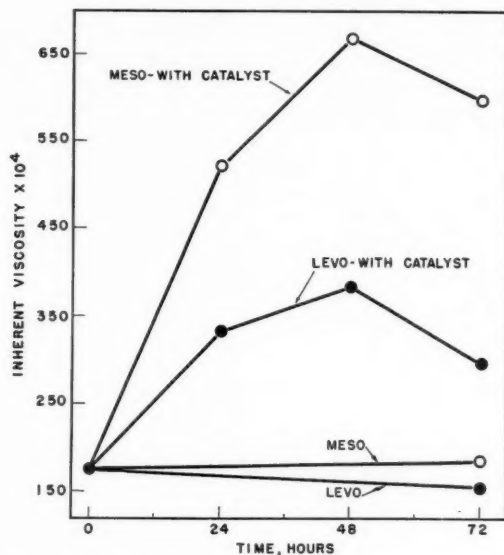


FIG. 2. Inherent viscosity vs. time of formation of polyesters from cyclic monomers.

TABLE I
COMPARISON BETWEEN POLYMERIZATION AND HYDROLYSIS OF CYCLIC OXALATES

Monomer	Polymerization	Hydrolysis
Ethylene oxalate (1)	Spontaneous at room temperature	Instantaneous with warm dilute alkali
Monomethylethylene oxalate (1)	When heated to 140°C. for eight hours	No data available
Dimethylethylene oxalate	Only when heated to 110°C. in presence of catalyst	50% hydrolysis instantaneous; complete in 30-35 days

rapid hydrolysis of the cyclic monomer and slow hydrolysis of the hydroxy acid are correlated with a depressed rate of polymerization. The methyl-substituted lactones investigated by Hollo (7) showed rates of hydrolysis depressed below those of corresponding unsubstituted compounds, but in every instance the methyl group was in a different position on a dissimilar ring. At present it is difficult to offer an explanation for the extremely rapid hydrolytic ring opening in the dimethylethylene oxalates.

Experimental

levo-2, 3-Butanediol, obtained from the fermentation of wheat by *Bacillus polymyxa* (9) was redistilled to $n_D^{25} = 1.4310$, $[\alpha]_D^{25} = -12.76$. *meso*-2, 3-Butane-

diol, produced by *Aerobacter aerogenes*, was redistilled to $n_D^{25} = 1.4340$, $[\alpha]_D^{25} = +1.78$ (12). Eastman ethyl oxalate, $n_D^{22.5} = 1.4089$, was used without further purification.

levo-Dimethylethylene Oxalate

The method of preparation has been previously described (14). Approximately 50 gm. of the cyclic monomer purified by repeated vacuum sublimation, had the following properties:

Calc. for $C_6H_8O_4$: C, 50.00; H, 5.55. Found: C, 50.29, 50.45; H, 5.37, 5.56. Melting range, 97.1° to 100.5°C.*; $\alpha_D^{25} = +9.14$ ($c = 3.61$ in chloroform); $+23.31$ ($c = 5.15$ in ethyl acetate); $+24.58$ ($c = 5.29$ in acetone). Molecular weight (theoretical), 144; observed values (Rast), 139, 145, 145.

meso-Dimethylethylene Oxalate

The *meso*-cyclic oxalate was prepared by the method described for the *levo*-monomer (14). The Rast molecular weight was 154 (observed values: 150, 151, 156, 157, 158: theoretical, 144). Calc. for $C_6H_8O_4$: C, 50.00, H, 5.55. Found, C, 50.22, 50.42; H, 5.35, 5.42. Melting range, 78.4°-80.4°C.: $\alpha_D^{25} = -0.465$ ($c = 2.68$ in acetone).

To determine the hydrolysis constant, 0.50 gm. of the cyclic monomer was dissolved in 5 ml. of redistilled reagent acetone. The acetone solution was added to carbon dioxide-free distilled water in a 500 ml. volumetric flask, made to volume, mechanically stirred, and maintained at $25.0^\circ \pm 0.2^\circ\text{C}$. in a water bath. At intervals a 10 ml. aliquot was removed and titrated with a 0.01 *N* sodium hydroxide to the phenolphthalein end point.

Polymerization of 0.2 gm. samples of the monomers, to each of which a trace of anhydrous potassium carbonate was added, were carried out in 10×30 mm. test tubes under nitrogen at 110°C .

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* All temperatures are corrected.

CUPRIETHYLENEDIAMINE AS A REAGENT FOR HEMICELLULOSE SEPARATION FROM WHEAT STRAW HOLOCELLULOSE¹

By V. D. HARWOOD

Abstract

Wheat straw and wheat straw holo cellulose were dispersed in aqueous cupriethylenediamine solutions and fractionated by graded precipitation with acid and alcohol. From the holo cellulose a 25.4% recovery of a hemicellulose containing negligible quantities of hexoses was achieved. The corresponding product from wheat straw was contaminated with both lignin and cellulose but a comparison of the chemical compositions of the two hemicelluloses showed that the acid chlorite used for delignification had caused very little hydrolytic action. The acetate of the hemicellulose from holo cellulose was fractionated from chloroform solution by the addition of petroleum ether into a series of fractions and sub-fractions. Analysis of representative fractions from this series led to the conclusion that the hexoses present were not chemically combined with pentosan. Molecular weights were determined by periodate oxidation, the Signer isothermal distillation method, and from the lowering of the vapor pressure of their chloroform solutions and showed that the hemicellulose molecules were relatively small (mol. wt. < 10,000). The decreasing ratio of xylose to arabinose in the fractions of lower molecular weight indicated increasing chain branching.

Introduction

Norman (17) has defined hemicelluloses as "alkali-soluble polysaccharides, hydrolyzable by dilute acids to component sugars and sugar acids". This definition includes various mixtures of amorphous polyuronide hemicelluloses and also short chain cellulosans derived from the cellulose micelles. On the basis of this definition it is not surprising to find that the conventional procedure for hemicellulose isolation has usually involved the extraction of the plant material with cold dilute alkali followed by acidification of the extract and subsequent precipitation of the hemicelluloses, with or without the addition of ethanol or other organic solvents.

This general procedure suffered from the rather serious drawback that the hemicelluloses thus isolated were contaminated with alkali-soluble lignin. To surmount this difficulty, plant material has been delignified by either alternate treatments with chloride dioxide or chlorine and organic bases (22, 24, 32) or by the action of acid chlorite (14, 33, 34). The resulting holo cellulose is then subjected to milder solvent treatment for the extraction of hemicelluloses (31). Complete delignification of holo cellulose can be achieved, however, only with concurrent loss of carbohydrate material (2, 14, 34). The nature of the degradative action of acid chlorite is not yet understood. Using wheat straw holo cellulose as a starting material, Adams and Castagne (3) and Bishop and Adams (4) have been able to remove 25.3% and 27.6% of the holo cellulose respectively by successive extractions with solvents ranging from cold water to 2% aqueous potassium hydroxide. Although the compositions of these fractions varied considerably, D-xylose, L-arabinose, and D-glucose were found

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in all and D-galactose in many of them. A hexuronic acid was also present. Recent work by Adams (1) in these laboratories has shown that the arabinose molecules are present in side chains.

In the present investigation the problem of hemicellulose isolation was approached by dispersing the holocellulose from wheat straw in cupriethylene-diamine and separating it into somewhat impure cellulose and hemicellulose fractions by precipitation of the former with acid. This method has been applied to the fractionation of cotton and flax celluloses by Straus and Levy (28, 29) but is new to the holocellulose field although cuprammonium hydroxide has been used by Haas in increasing concentrations to fractionate the holocelluloses of beech and pine wood (9, 10).

Materials and Methods

Commercial cupriethylenediamine solution which was one molar with respect to copper was obtained in 1 gal. bottles from the Ecusta Paper Corporation, Pisgah Forest, N.C. Deterioration of the reagent was prevented by storing under an atmosphere of nitrogen. Pectin- and extractive-free wheat straw holocellulose that had been isolated by chlorite delignification (2) was provided by G. A. Adams of this laboratory. Pentoses were determined by distillation with 12% hydrochloric acid and the evolved furfural was measured by the bromine oxidation procedure of Hughes and Acree (12). Uronic acid anhydride was determined by the method of Tracy (30); methoxyl by the microprocedure of Clarke (8), and acetyl content by alkali saponification and back titration with standard acid. Lignin was determined by the 72% sulphuric acid procedure of Ritter, Seborg, and Mitchell (23). Reducing sugars were determined by the method of Somogyi (25) and the component sugars of the various polysaccharides, after acid hydrolysis, were separated by paper chromatography. Periodate oxidation by the method of Halsall *et al.* (11), the Signer isothermal distillation method (8), the lowering of the vapor pressure of their solutions (21), and viscosity measurements were used to estimate the approximate molecular weights of individual fractions. Moisture and ash were determined at 110° and 550°C. respectively and, unless otherwise noted, all analyses were on an ash-free, moisture-free basis.

Experimental Procedures and Results

The investigation proceeded along three lines; separation of holocellulose into cellulose and hemicellulose components; application of the same procedure to wheat straw; fractionation of the hemicellulose derived from the holocellulose into subfractions, some of which were used for molecular weight determinations.

Preparation of Cupriethylenediamine Hemicellulose From Holocellulose

Straus and Levy (29) dissolved cellulose to the extent of 1 gm. per 100 ml. of 0.5 M cupriethylenediamine but preliminary experiments on wheat straw holocellulose showed that it was soluble at about half this concentration. On

this basis approximately 100 gm. of wheat straw holocellulose was dispersed in 4.5 liters of 0.5 *M* cupriethylenediamine in an atmosphere of nitrogen and diluted with an equal volume of water. An insoluble material (Fraction I) was recovered by centrifuging and washing with water. This residue and a further quantity of holocellulose were retreated with 4.5 liters of 0.5 *M* cupriethylenediamine and the procedure repeated until eventually 328.6 gm. of holocellulose had been dispersed in 27 liters of 0.25 *M* cupriethylenediamine solution. The whole of Fraction I was then removed by centrifuging. The addition of 1.5 liters of 8 *N* hydrochloric acid to the centrifugate reduced the pH from 12.8 to 11.5 and caused the precipitation of a gelatinous "cellulose" (Fraction II). This product was washed with 50% ethanol, subsequently deashed with 3% hydrochloric acid in 50% ethanol and dried through ethanol and ether on a centrifuge. A second lot of 1.5 liters of 8 *N* hydrochloric acid was added to the 42 liters quantity of centrifugate and acidic washings from the gelatinous "cellulose" precipitate to further reduce the pH to 4.3 and to cause the precipitation of Fraction III, a granular material. Finally the combined 45 liters of washings and centrifugates was neutralized with 8 *N* potassium hydroxide and concentrated *in vacuo* at 40-50°C. to 6.7 liters. To each liter of this solution 4.5 liters of 95% ethanol and 0.4 liters of 4 *N* hydrochloric acid were added to precipitate Fraction IV, a "hemicellulose" that was recovered by centrifuging, washed with 1.5% hydrochloric acid in 75% ethanol, and then dried through ethanol and ether. All four fractions were analyzed for pentosan and uronic acid content. The yields and analytical data are recorded in Table I.

From Wheat Straw

A 16.0 gm. sample of the pectin-free and extractive-free wheat straw was shaken for 16 hr. with 375 ml. water and an equal volume of 1 *M* cupriethylenediamine. An insoluble residue was recovered by centrifuging and washed successively with water, 30 ml. of 8 *N* hydrochloric acid, and finally with ethanol and ether. This residue was termed "lignin". The pH of the centrifugate and washings was reduced to 6.5 and a precipitated "cellulose" fraction recovered. After neutralization with aqueous potassium hydroxide, the 4 liters of washings and centrifugate from the "cellulose" precipitation were concentrated *in vacuo* at 40-50°C. to 625 ml., and 2.5 liters of 95% ethanol was added along with sufficient 8 *N* hydrochloric acid to reduce the pH to 4. A "hemicellulose" fraction was thus obtained. The analyses of these three fractions are given in Table II.

Hydrolysis of Fractions from Wheat Straw and Holocellulose

Three different procedures were used for the hydrolysis of the various fractions described in Tables I and II.

(a) A 50 mgm. sample of the hemicellulose from the holocellulose was hydrolyzed by 5 ml. of 0.5% sulphuric acid in a boiling water bath. After a small insoluble residue had been recovered by centrifuging the supernatant liquor was analyzed directly by paper chromatography.

TABLE I
COMPOSITION OF FRACTIONS PREPARED FROM WHEAT STRAW HOLOCELLULOSE
BY CUPRIETHYLENEDIAMINE

Material examined	Dry weight, gm.	Ash, %	Ash-free wt., gm.	Recovery of original, %	Pentosan, *		Uronic acid anhydride	
					%	Gm.	%	Gm.
Holocellulose	306.7	2.1	300.2		29.3	88.0	4.9	14.7
Fraction I	8.6	17.0	7.2	2.4	4.1	0.3	2.7	0.2
Fraction II	184.3	0.6	183.2	61.0	9.7	17.8	2.6	4.8
Fraction III	6.0	1.1	5.9	2.0	41.9	2.5	4.0	0.2
Fraction IV	80.2	4.9	76.3	25.4	82.9	63.3	7.3	5.8
Totals			272.6	90.8		83.9		11.0

Recovery based on holocellulose, %

95.3

74.8

* Corrected for pentosans liberated from uronic acids.

TABLE II
COMPOSITION OF FRACTIONS PREPARED FROM WHEAT STRAW BY CUPRIETHYLENEDIAMINE

Material examined	Dry wt., gm.,	Ash, %	Ash-free wt., gm.	Recovery of original, %	Pentosan, *		Uronic acid anhydride		Lignin,	
					%	Gm.	%	Gm.	%	Gm.
Wheat straw	14.91	0.9	14.77		30.0	4.43	6.5	0.96	20.0	2.95
Fraction "Lignin"	4.22	1.7	4.15	28.1	11.9	0.49	1.2	0.05	23.7	0.98
"Cellulose"	6.40	1.5	6.30	42.7	25.5	1.61	0.8	0.05	7.9	0.50
"Hemicellulose"	3.22	3.6	3.10	21.0	74.9	2.32	5.3	0.16	12.7	0.39
Totals			13.55	91.8		4.42		0.26		1.87

Recovery based on wheat straw, %

99.8

27.1

63.4

* Corrected for pentosans liberated from uronic acids.

(b) The procedure for the other three fractions from the holocellulose was to treat a 100 mgm. sample with 10 ml. of 0.5% sulphuric acid. When the reducing value of the hydrolyzate reached a constant value, it was removed by centrifuging and the residue rehydrolyzed with 10 ml. of 4% sulphuric acid, at 100°C. At the completion of the second hydrolysis the hydrolyzates were neutralized with barium carbonate, the precipitate removed and washed with warm water, and the solution analyzed by paper chromatography. The residues remaining, which amounted to from 45-80 mgm. were treated with 1.0 ml. of cold 72% sulphuric acid and left for 16 hr. at 5°C. Hydrolysis was completed by adding 37.6 ml. of water and heating in a boiling water bath for four hours.

Barium carbonate was again used to neutralize the sulphuric acid. Treatment of the concentrated hydrolyzate with a washed culture of resting cells of *Torulopsis utilis* var. *thermophila* (N.R.C. 862) preferentially fermented the glucose. Reducing-power determinations before and after fermentation and paper chromatography of the glucose-free solution led to a complete analysis of the products.

(c) An alternate procedure that resulted in a more complete recovery of sugars in the same three holocellulose fractions was to treat 250 mgm. samples overnight with 1.1 ml. of cold 72% sulphuric acid, then to boil under reflux with 45 ml. of water to complete the hydrolysis.

The various fractions which had been prepared from wheat straw were analyzed by Method (c) using 1 gm. samples and correspondingly larger amounts of sulphuric acid. Each solution was then made up to 1 liter, a 100 ml. aliquot taken, and neutralized with barium carbonate. After removal and washing of the precipitate, the filtrate and washings were concentrated to 10 ml. and analyzed by paper chromatography.

Analysis of Constituent Sugars in Hydrolyzates

The chromatographic procedure used in these laboratories was developed by Perlin (18) after a consideration of various methods. Xylose, arabinose, and glucose were the only sugars qualitatively detected and quantitatively estimated in the wheat straw (Table III) and holocellulose (Table IV) fractions. These results confirmed the previously established fact (3, 4) that xylose and arabinose are the main constituent sugars of the hemicellulose from wheat straw holocellulose.

Fractionation of Hemicellulose Prepared from Holocellulose

To estimate the molecular weight distribution of the hemicellulose prepared by the cupriethylenediamine procedure, it was necessary to fractionate the product into as many distinct fractions as possible. Trial experiments using water or cupriethylenediamine failed to yield any distinct separations, but acetylation followed by precipitation with petroleum ether from chloroform solution showed more promise.

TABLE III
CONSTITUENT SUGARS OF WHEAT STRAW FRACTIONS
(Based on weight of nonlignin part, by difference)

Constituent sugars	"Lignin"	"Cellulose"	"Hemicellulose"
Anhydroarabinose, %	2.6	6.6	9.7
Anhydroxylose, %	9.7	21.5	65.8
Anhydroglucose, %	76.5	53.5	4.5
Total, %	88.8	81.6	80.0
Xylose: arabinose	3.7: 1.0	3.3: 1.0	6.8: 1.0
Glucose: pentose	6.2: 1.0	1.9: 1.0	1.0: 16.8

TABLE IV
 CONSTITUENT SUGARS OF HOLOCELLULOSE FRACTIONS

Fractions	Hydrolysis method	Anhydrosugars, %			Total, %	Xylose Arabinose	Glucose Pentose
		Arabinose	Xylose	Glucose			
I	Complete (c)		1.4	80.4	81.8		57:1.0
II	Graded (b)	0.7	10.0	56.1	69.7	14.3:1.0	4.1:1.0
	Complete (c)	1.7	8.8	82.9	93.4	5.2:1.0	7.9:1.0
III	Graded (b)	3.4	38.9	32.6	74.9	11.4:1.0	1.0:1.3
	Complete (c)	2.0	38.7	35.0	75.7	19.4:1.0	1.0:1.2
IV	Complete (a)	8.8	71.9		80.7	8.2:1.0	

Acetylation of Hemicellulose

A quantity of hemicellulose equivalent to 20.0 gm., ash- and moisture-free, was dispersed in 354 ml. (400 gm.) of formamide by stirring for 1 to 1.5 hr. at 60 to 70°C. (6). To this suspension were added successively 400 ml. of dry pyridine and 400 ml. of benzene, the latter to maintain the system as a fluid instead of as a gel. Acetic anhydride was added over a period of 1.5 hr. in four lots of 32 ml. and the solution was stirred for 16 hr. The acetate was recovered by pouring the reaction mixture into 6 liters of ice water, followed by stirring to decompose the acetic anhydride. The precipitated acetate was washed with water, 3% hydrochloric acid, more water, then ethanol and yielded 34.7 gm. of dry acetate (38.7% acetyl). To reacetylate, 300 ml. of benzene and an equal volume of pyridine were added to the product which was then heated and stirred at 70°C. for 30 min. The addition of 300 ml. of acetic anhydride and further stirring for 40 hr. at room temperature and for 16 hr. at 50-55°C. completed the reacetylation. The yield was 34.0 gm. (39.6% acetyl).

Fractionation of Hemicellulose Acetate

Almost the total yield of acetate, viz. 33.7 gm., was dissolved in 3400 ml. of chloroform and successive fractions precipitated by the addition of increasing quantities of petroleum ether (b.p. 40-60°C.). Each precipitate was centrifuged and washed with a solvent mixture of the same approximate composition as the supernatant liquor before a final washing with pure petroleum ether. In this manner 18 fractions and a small residue were recovered from the original solution. The optical rotation of all but the first fraction was readily obtained using 1% solutions in chloroform. These solutions were then used for viscosity determinations at 0.5, 0.25, 0.125, and 0.063% concentration in chloroform using an Ostwald-Cannon-Fenske viscometer (A.S.T.M. 50) in a water bath at 25°C. \pm 0.02°C. The plots of η_{sp}/C versus C or of $\ln \eta R/C$ versus C were straight lines for all but the first five fractions, where C was expressed in terms of grams per liter of solution. When extrapolated to zero concentration the intrinsic viscosities $[\eta]$ were derived from the graphs.

Refractionation of Hemicellulose Acetate Fractions

Fraction I was dispersed in chloroform and subfractions 1-6 precipitated from it by successive additions of petroleum ether. Fractions 8 to 11 inclusive were refractionated to determine whether any greater differences might be apparent in their optical rotations and intrinsic viscosities. This was done by dissolving Fraction 8 in chloroform to make a 1% solution and then adding petroleum ether to cause the precipitation of Subfraction 7. To the centrifugate and washings of Subfraction 7, a 3% solution of 9 was added and then more petroleum ether. This was repeated until Fractions 8 to 11 were recovered as Subfractions 7-14. In Table V are tabulated the data on viscosity, rotation, and yield of all fractions and subfractions. On the basis of similar rotations and intrinsic viscosities, Fractions 4 and 5; 6, 7, and Subfraction 7; Subfractions 8-11 were combined to form the composite fractions A, B, and C respectively. Samples of certain representative fractions, viz. 13, 14, 15, 16 and Subfractions 1, 4, and 13 and the composite fractions A, B, C, were deacetylated with a calculated 10% excess of potassium hydroxide in an acetone dispersion of the acetate and hydrolyzed by 0.5% sulphuric acid. Paper chromatography led to the results recorded in Table VI.

Molecular Weight Determinations

Physical Methods

Attempts were made to determine the molecular weights of a few acetates from the lowering of the vapor pressure of their solvents (21). Chloroform, the

TABLE V
PHYSICAL CONSTANTS OF HEMICELLULOSE ACETATE FRACTIONS AND SUBFRACTIONS

Fractions	Weight, gm.	$[\alpha]_D^{20}$ in chloroform	Intrinsic viscosity* $[\eta]$	Subfractions	Weight, gm.	$[\alpha]_D^{20}$ in chloroform	Intrinsic viscosity* $[\eta]$
1	10.04	..	0.060	From	1	1.50	..
2	5.65	-104°	0.068	Fraction	2	3.51	..
3	1.55	-109	0.054	I	3	2.09	..
4	1.23	-111	0.051		4	0.91	-110°
5	0.99	-108	0.056		5	0.53	-117
6	1.53	-114	0.059		6	0.29	-108
7	0.78	-112	0.051		7	0.90	-108
8	2.08	-114	0.052	From	8	0.85	-106
9	0.67	-114	0.048	Fraction	9	0.50	-102
10	0.75	-113	0.045	tions	10	1.18	-109
11	1.93	-115	0.040	8 to	11	0.35	-102
12	1.82	-111	0.033	11	12	0.60	-108
13	1.26	-111	0.026	inclusive	13	0.45	-114
14	0.68	-105	0.020		14	0.06	..
15	0.74	-100	0.015				
16	0.49	-81	0.012				
17	0.09	-81	0.011				
18	0.06	-58					
19	1.16						

Total (1 to 19) 33.50 (99.5% recovery)

* Mean of values from the extrapolations of η_{sp}/C and $\ln \eta R/C$ vs. C curves.

TABLE VI
COMPOSITION OF THE DEACETYLATED HEMICELLULOSE ACETATE FRACTIONS
AND SUBFRACTIONS

	Original hemicellulose, %	Constituent anhydrosugars, %			Xylose Arabinose
		Arabinose	Xylose	Hexoses	
Fractions					
A	6.6	6.7	70.4	10.5:1.0
B	9.5	7.3	72.7	10.0:1.0
C	8.6	7.0	63.6	9.1:1.0
13	3.7	8.4	64.9	7.7:1.0
14	2.0	12.0	81.2	6.8:1.0
15	2.2	11.4	74.8	6.6:1.0
16	1.5	16.9	58.7	6.3	3.5:1.0
Subfractions					
1	4.5	8.7	74.4	8.6:1.0
4	2.7	7.1	80.4	11.3:1.0
13	1.3	9.5	76.3	8.0:1.0

only acetate solvent with a reasonably high vapor pressure at room temperature, was freed of ethanol by passing it through a column of silica gel. Because of either the photolysis of the solvent or the use of highly concentrated solutions in the apparatus, few values could be obtained. A second approach was by Signer's isothermal distillation method (8). Solvent decomposition might also have been the cause of the limited success of this technique since it required chloroform solutions of the acetates and of a reference compound, sucrose octaacetate. Here the likelihood of decomposition of the chloroform was enhanced by the extensive period required for equilibrium to be established.

Chemical Method

Periodate oxidation is the basis of an end-group method for the determination of molecular weights (5). The procedure adopted in the present investigation was to deacetylate sufficient material to yield 150 mgm. samples of each fraction. To each sample, in an actinic glass flask, was added 100 ml. of water and 20 ml. of a solution made by neutralizing 6.0 gm. of periodic acid with 0.1 *N* sodium hydroxide using bromcresol purple as indicator (16). The samples and a blank of the same composition were shaken at 15°C. for two weeks. Aliquots were analyzed for periodate consumed after 2, 3, 4, 6, 9, and 13 days and for formic acid produced after 9 and 13 days only. On the assumption that one mole of formic acid was formed from a nonreducing xylose end-group, and that two moles were liberated from the reducing end, a molecular weight was calculated from the milliequivalents of formic acid formed at the level of maximum oxidation. The latter was reached after nine days when almost one mole of oxygen per mole of anhydroxylose was consumed. In Table VII the molecular weights determined by all three methods are summarized.

TABLE VII
DEGREES OF POLYMERIZATION OF HEMICELLULOSE ACETATE
FRACTIONS

Fraction	Vapor pressure lowering method	Signer method, mean of three values	Mean of physical methods	Periodate oxidation method	Intrinsic viscosity $[\eta]$	$K_m \times 10^{-4}$	
						Mean of physical methods	Periodate oxidation
A	31.5	31.5	41.8	0.052	16.5	12.4
B	22.0	25.8	23.9	45.1	0.057	23.8	12.6
C	21.8	34.3	28.1	56.7	0.048	17.1	8.5
13	20.0	20.0	39.2	0.033	16.5	8.4
15	10.9	15.6	13.3	22.4	0.019	14.3	8.5
Subfraction 13	19.2	19.2	37.0	0.034	17.7	9.2

Discussion

Numerous investigators (19, 20) have postulated that lignin is chemically combined with carbohydrates in lignified cell walls. As to the linkage involved, the usual suggestions are acetal or ether-like combinations or an ester-like union between an acidic group in the lignin complex and an hydroxyl group of the carbohydrate. A perusal of Table II shows that good recoveries of pentosans and of the components of the original straw were obtained but that considerable losses of uronic acid and lignin were sustained in this fractionation. The loss of uronic acid cannot be explained on the basis of its association with the pentosans (17) which were completely recovered in this case. The uronic acid might, however, be associated or combined with that portion of the lignin or nonpentosan carbohydrate that remained in solution in the cupriethylene-diamine left after removal of the "hemicellulose". No direct evidence is available to prove that the lignin in the various fractions is combined with carbohydrate since the two components might simply have been coprecipitated. With holocellulose (Table I) it is evident that the not inconsiderable loss of uronic acid could be related to the incomplete recovery of both pentosan and nonpentosan carbohydrate. Unfortunately, no way could be found to recover carbohydrates from the mixed cupric chloride and ethylenediamine hydrochloride aqueous alcohol solution left after the "hemicellulose" precipitation.

The composition of the carbohydrates of both the straw and its holocellulose show a definite trend from fractions high in glucose and low in pentose, i.e. a ratio of cellulose to hemicellulose greater than one, to fractions that have little or no glucose, i.e. cellulose. During this fractionation into cellulose and hemicellulose, the composition of the pentosans within the fractions was also changing. The low xylose to arabinose ratio in "lignin" changed to a "hemicellulose" with a 7 to 1 ratio and Fraction IV from holocellulose with an 8 to 1 ratio. These trends were discernible even though the analytical data varied considerably because of the use of 72% sulphuric acid as a hydrolytic agent.

The recovery of sugars based on the original carbohydrate was low, particularly in the graded hydrolyses (*b*) of the holocellulose fractions although the amounts extracted from the paper chromatograms were at least 80% of those placed on the papers. Presumably 72% sulphuric acid either was not completely hydrolyzing the carbohydrate material or was decomposing some of the monosaccharides. The quantities of pentoses found by both methods were approximately the same as the content of pentosans. The higher xylose to arabinose ratio in holocellulose hemicellulose (8:1) than in the wheat straw "hemicellulose" (7:1) suggests that in the preparation of the holocellulose by the acid chlorite method about 8% of the arabinose had been removed. The cupriethylenediamine treatment is not expected to remove more arabinose from one product than the other.

From similarities in the characteristics of the fractions and subfractions (Tables V and VI), the hemicellulose acetates may be divided into three main groups.

The first group, consisting of Subfractions 1, 2, and 3, and amounting to 21.1% of the total, is characterized by the formation of turbid suspensions in chloroform that forestall any attempts to determine their optical rotation or viscosity. A fairly high ratio of xylose to arabinose indicates a medium degree of chain branching since recent work of Adams (1) in these laboratories has shown that the arabinose units are only present as branches off a main xylan chain.

The second group contains the main bulk of the fractions from 2 to 13 and also the reprecipitated Subfractions 4 to 14. Within this group (72% of the total) the composite fractions *A*, *B*, and *C* (24.7% of the total acetate) have very similar intrinsic viscosities and optical relations. Their chemical analyses show marked similarities with respect to constituent groups:

Fractions	Methoxyl, %	Uronic acid anhydride, %
<i>A</i>	4.2	5.8
<i>B</i>	4.2	4.2
<i>C</i>	3.1	4.8

and also a lower ratio of xylose to arabinose indicating more chain branching (Table VI).

The remaining fractions tail off to very small quantities with lower rotations, smaller intrinsic viscosities, and ratios of xylose to arabinose concordant with a high degree of chain branching particularly in Fraction 16 where two xylose units in seven would be expected to have an arabinose group attached. Since measurable quantities of glucose and galactose were detected only in Fraction 16, it is highly probable that as much as 98% of the hemicellulose can be isolated free of hexose. No chemical combination of hexose and pentosan is likely to have pre-existed in the holocellulose since in that event the more

soluble hexose triacetates would be expected in all the fractions. The low yield of sugars from the hydrolyses of these fractions is probably due to incomplete hydrolysis of uronic acid di- and trisaccharides under the conditions of the experiment, rather than to the chromatographic procedure in which recovery was between 87 and 99% in Fractions *A* to *C*.

In Table VII the molecular weights, in the form of degrees of polymerization (D.P.), are recorded for 6 of the 10 hemicellulose acetate fractions. The D.P. of each of the acetates was calculated on the basis of a xylose acetate unit containing 39.6% acetyl, the average for the acetyl content of the whole hemicellulose acetate. Single values only were obtained by the vapor pressure lowering method (21) and by periodate oxidation. The chemical method gave consistently higher values than those obtained by physical methods. Both the results by physical methods and those by periodate oxidation may be related to the mean intrinsic viscosities to arrive at values for Km in the equation

$$\eta_{sp}/C = KmP \quad (15)$$

where η_{sp}/C is the specific viscosity divided by the concentration extrapolated to zero concentration, i.e. the intrinsic viscosity $[\eta]$, P is the degree of polymerization, and Km is the Staudinger constant. The Km figures recorded in the last two columns of Table VII are not constant in view of the differences in chemical composition of the fractions (*cf.* Table VI). Periodate oxidation results, however, do at least show a break in continuity between the Km values of the less branched fractions with 10 to 1 ratios of xylose to arabinose and the more branched fractions with 8 to 1 ratios.

Several investigators (3, 7, 15), when dealing with hemicellulose diacetates, have used Staudinger's Km values of 11×10^{-4} and 5.3×10^{-4} for cellulose triacetate in chloroform solution (26, 27). Husemann (13) in his work on wheat straw xylan established Km values ranging from 4.2 to 6.6×10^{-4} for various derivatives that did not include the diacetate. The variations in Km values obtained in the present investigation confirm the results of other workers and suggest that caution should be used in applying these constants to viscosity data for molecular weight determinations of hemicellulose derivatives.

From viscosity measurements Husemann (13) established that extensive chlorine dioxide treatment caused a 20% chain length degradation in wheat straw xylan as compared to xylan isolated without the use of chlorine dioxide. More than 80% of the latter had a D.P. greater than 145 determined viscometrically, figures far exceeding the percentage and D.P. of the longest chain material in the present investigation, viz. some 20% with a D.P. greater than 55 in the first group. In the second group the D.P. range was from 55 to 37 and the values for the remainder of the acetates fell below 37 down to about 14. A comparison with Husemann's values lead to the conclusion that either the use of acid chlorite, or of cupriethylenediamine, or both, caused more degradation than the use of chlorine dioxide. Such a conclusion is based, of course, on the assumption that the starting materials contained hemicelluloses with the same degrees of polymerization. A study of the degradation of wheat straw holocellulose by acid chlorite is warranted.

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INFLUENCE DE GAZ ETRANGERS SUR LA FLAMME FROIDE DE L'ETHER¹

LUDOVIC OUELLET ET CYRIAS OUELLET

Sommaire

Utilisant la méthode photo-électrique déjà décrite (4), on a étudié l'influence de l'addition d'hydrogène, d'azote, de vapeur d'eau, d'anhydride carbonique, de formaldéhyde et d'acétaldéhyde sur la flamme froide de l'éther. Les premiers se comportent comme des diluants. La formaldéhyde agit comme un inhibiteur. Le remplacement d'une partie de l'éther par de l'acétaldéhyde ou l'addition des produits d'une réaction précédente prolonge la période d'induction sans altérer la quantité de lumière émise.

Introduction

Les diverses façons dont les caractéristiques de la flamme froide de l'éther éthylique sont influencées par les variables: température, pression, composition du mélange combustible et diamètre du récipient ont été décrites dans des travaux récents (2, 3, 4). L'addition de gaz étrangers exerce aussi des effets considérables, susceptibles de nous renseigner sur certains aspects du mécanisme de ce phénomène. Quelques expériences effectuées en présence d'oxyde d'azote et de plomb tétraéthyle ont été décrites sommairement (2), mais l'étude détaillée des effets de ces substances reste à faire. Le présent travail contient l'exposé des résultats obtenus avec trois catégories de gaz: (1) les gaz neutres ou simples diluants, dont l'action permet dans certains cas de distinguer entre une réaction thermique et une réaction en chaînes, (2) les inhibiteurs, en particulier les aldéhydes qui sont en même temps des produits intermédiaires de la réaction et finalement, (3) les produits mêmes de la flamme froide, phénomène à la fois autocatalytique et auto-inhibé.

Toutes les expériences mentionnées ici ont été effectuées à 215°C. avec des mélanges d'éther éthylique et d'oxygène en proportions équimoléculaires. On s'est servi de la méthode déjà décrite (4), qui consiste à produire une lueur statique en introduisant brusquement le mélange gazeux dans un récipient en Pyrex maintenu à une température appropriée et à mesurer l'émission lumineuse au moyen d'une cellule photo-électrique et d'un oscillographe cathodique. Les récipients utilisés étaient des tubes de Pyrex de 130 mm. de longueur et de 46 mm. de diamètre. Les oscillogrammes représentés sur les figures portent une échelle de temps en secondes et une échelle d'intensités arbitraire mais uniforme. Autant que possible, les oscillogrammes sont caractérisés par les paramètres commodes suivants: l'émission lumineuse intégrale A , la hauteur h_2 de la dernière crête et sa position t_2 sur l'axe des temps, ainsi que la durée totale approximative t de la lueur.

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Résultats

Addition de gaz neutres

Le Tableau I indique les conditions dans lesquelles ont été effectuées quelques expériences comportant l'addition d'azote, d'hydrogène, d'anhydride carbonique et de vapeur d'eau.

TABLEAU I

INFLUENCE DE GAZ NEUTRES SUR LES FLÂMMES FROIDES DE MÉLANGES ÉQUIMOLÉCULAIRES D'ÉTHÉR ET D'OXYGÈNE À 215°C. PRESSIONS PARTIELLES P_{Et} , P_{O_2} ET P_G DE L'ÉTHÉR, DE L'OXYGÈNE ET DU GAZ NEUTRE, ÉMISSION INTÉGRALE A , HAUTEUR h_2 DE LA DERNIÈRE CRÊTE ET DURÉE t DE LA LUEUR

Expérience No.	P_{Et}	P_{O_2}	P_G	A , mm. ²	h_2 , mm.	t , sec.
	mm. Hg					
N ₂						
1032	38	38	9	800	18	0.92
683	38	38	0	980	21	1.02
1031	35	35	7	660	16	0.83
686	35	35	0	925	20	0.96
1179	16	16	16	150	0	0.35
1168	16	16	0	200	2	0.52
1177	21	21	21	410	6	0.87
690	21	21	0	268	8	0.79
1193	28	28	61	800	18	0.87
1044	29	29	0	570	18	0.77
1194	23	23	50	600	12	0.96
1164	24	24	0	420	13	0.71
H ₂						
1109	29	29	4.5	645	18	0.77
1091	29	29	0	550	16	0.78
1110	24	24	3.5	530	15	0.82
CO ₂						
965	28	28	28	360	10	0.69
688	28	28	0	600	13	0.82
970	24	24	24	280	10	0.75
972	19	19	19	150	0	0.38
961	27	27	27	300	8	0.65
1165	27	27	0	525	12	0.70
H ₂ O						
1024	28	28	6	450	13	0.78
1025	26	26	6	400	12	0.75
1026	19	19	4	240	10	0.72
1167	18	18	0	270	11	0.75
1028	40	40	9	690	19	0.80
684	40	40	0	1050	24	1.04
1029	44	44	10	840	21	0.92

On voit les principaux effets de l'azote sur la Figure 1, où les courbes pointillées obtenues en présence de ce gaz sont juxtaposées aux courbes pleines données par des expériences témoins. En aucun cas la période d'induction ne semble affectée de façon appréciable. A pression totale relativement élevée, la présence de 10% d'azote exerce une faible inhibition qui affecte surtout la première crête. Aux pressions plus basses, la seconde crête est fortement inhibée (1177) ou même supprimée (1179) par 33% d'azote, mais la première crête est accentuée, de sorte que l'émission intégrale est peu affectée. Comme le montre la Figure 1, la faible inhibition de l'émission intégrale par 10% d'azote se change en une augmentation nette lorsque la proportion de ce gaz atteint 52%. On voit aussi apparaître un prolongement de la durée totale, effet d'autant plus marqué que l'on opère à une pression plus élevée.

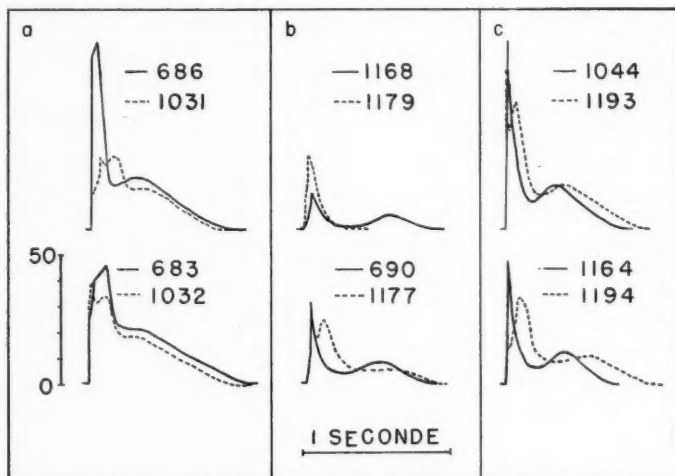


FIG. 1. Influence de l'addition d'azote sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène. (a). 10% N_2 en volume. (b). 33% N_2 . (c). 52% N_2 . Les oscillogrammes en traits pointillés obtenus en présence d'azote sont comparés à des oscillogrammes obtenus en l'absence d'azote. Les données apparaissent au Tableau I.

Quelques expériences en présence de 7% d'hydrogène indiquent que ce gaz se comporte comme un gaz neutre dont les effets (Fig. 2) sont très voisins de ceux de l'azote.

La vapeur d'eau et l'anhydride carbonique exercent aussi une inhibition semblable à celle de l'azote en faibles proportions. L'influence de 33% d'anhydride carbonique est environ le triple de celle de 10% d'eau (Fig. 3); ces deux gaz ont donc des pouvoirs inhibiteurs sensiblement égaux, qui sont d'ailleurs nettement supérieurs à ceux de l'azote et de l'hydrogène.

Addition d'aldéhydes

On sait que la luminescence des flammes froides est attribuée, à cause de son spectre (7), à la fluorescence de la formaldéhyde excitée produite au cours de

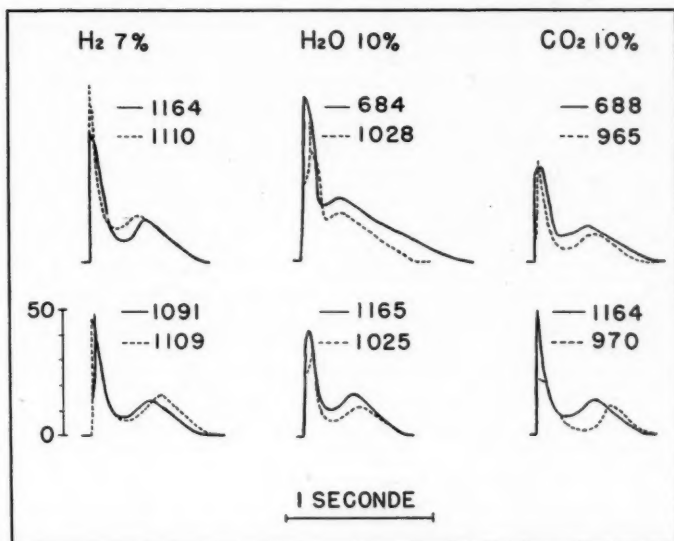


FIG. 2. Influence de l'addition d'hydrogène, d'eau et d'anhydride carbonique sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène à 215°C. Les oscillogrammes représentés en traits pointillés ont été obtenus en présence de ces gaz étrangers.

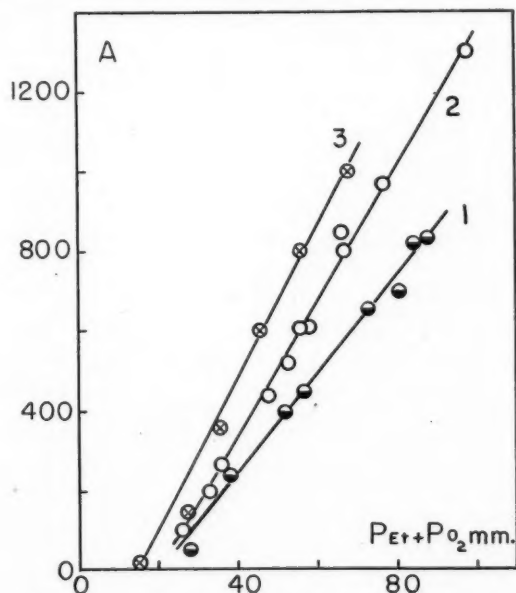


FIG. 3. Emission intégrale A d'une flamme froide d'un mélange équimoléculaire d'éther et d'oxygène en fonction de la pression d'éther et d'oxygène ($P_{Et} + P_{O_2}$). (1). En présence de 10% de vapeur d'eau, (2). En l'absence de gaz étrangers, (3). En présence de 52% d'azote.

la réaction. Cependant, l'oxydation de la formaldéhyde elle-même n'est accompagnée d'aucune émission lumineuse; au contraire, cette substance exerce une action inhibitrice (8) sur les flammes froides. La méthode photo-électrique a permis d'analyser quelques particularités de cette inhibition.

L'addition de formaldéhyde gazeuse, fraîchement préparée par chauffage de la paraformaldéhyde, produit trois effets principaux: prolongement de la période d'induction, inhibition de l'émission et déformation de l'oscillogramme. Le Tableau II contient des renseignements sur les flammes étudiées en présence de ce gaz; on y trouve quelques valeurs approximatives de la période d'induction, que notre dispositif actuel ne permet pas de mesurer avec précision. La Figure 4 montre quelques exemples de flammes inhibées et déformées. Toutes les pulsations sont amorties et retardées; en particulier, la crête initiale n'est plus aiguë et son sommet n'est plus atteint aussi soudainement. Aux pressions suffisamment basses, la dernière crête finit par disparaître (1347), comme dans les cas d'inhibition par les parois (4) ou par les gaz neutres.

TABLEAU II

INFLUENCE D'ALDÉHYDES SUR LES FLAMMES FROIDES DE MÉLANGES ÉQUIMOLÉCULAIRES D'ÉTHER ET D'OXYGÈNE À 215°C. τ EST LA PÉRIODE D'INDUCTION APPROXIMATIVE. LES AUTRES SYMBOLES ONT LA MÊME SIGNIFICATION QU'AU TABLEAU I

Expérience No.	P_{Et}	PO_2	P_G	A , mm. ²	t , sec.	τ , sec.
	mm. Hg					
HCHO						
995	37	37	4	570	0.79	1
685	38	38	0	970	1.02	0
994	43	43	5	950	1.00	1
1300	43	43	0	1090	1.03	0
1345	37	37	9	720	1.18	10
1347	27	27	6	320	1.02	10
1348	22	22	5	Aucune réaction		
CH ₃ CHO						
940	40	40	40	1175	0.94	1
1308	84	42	0	1340	0.90	0
941	36	36	36	910	0.73	1
1309	75	37	0	1110	0.89	0
943	27	27	27	660	0.61	1
1311	54	27	0	640	0.73	0
951	7	7	7	25	0.17	1

L'acétaldéhyde, comme l'éther, donne elle-même naissance à des flammes froides. Elle est d'ailleurs un produit intermédiaire de la flamme froide de l'éther, dans laquelle elle contribue vraisemblablement, comme précurseur, à l'émission lumineuse.

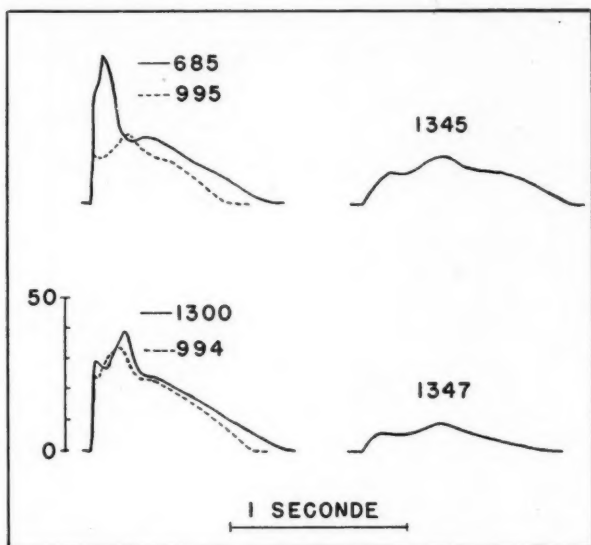


FIG. 4. Influence de la formaldéhyde sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène à 215°C. Les données apparaissent au Tableau II.

Comme nous l'avons vu (2), la flamme froide de l'acétaldéhyde a la même allure que celle de l'éther, mais est caractérisée par une durée un peu plus courte et est affectée d'une période d'induction plus longue. L'addition d'acétaldéhyde, distillée deux fois dans le vide, à un mélange d'éther et d'oxygène, impose à la flamme froide une période d'induction de l'ordre d'une seconde, mais ne modifie pas beaucoup la flamme qui apparaît ensuite, comme on peut le constater par l'examen des oscillogrammes de la Figure 5. Il semble que, contrairement à la formaldéhyde, l'acétaldéhyde contribue à l'émission lumineuse, après avoir inhibé une étape antérieure de la réaction. Il est même possible que la flamme de l'éther soit en réalité celle de l'acétaldéhyde, l'éther n'agissant que comme source de ce composé. En effet, si on remplace une partie de l'éther par de l'acétaldéhyde, on obtient des oscillogrammes dont ni la forme (Fig. 5) ni l'émission intégrale (Fig. 6) ne sont sensiblement altérées.

Addition des produits de la réaction

Si, au lieu d'évacuer complètement le récipient à la suite d'une réaction, on y laisse une partie des gaz à une pression partielle de quelques millimètres, l'introduction d'un mélange frais donne lieu à une nouvelle flamme qui est retardée et déformée mais dont l'émission intégrale est à peu près normale. La Figure 7 montre des oscillogrammes normaux et, à leur droite, ceux qui ont été enregistrés dans les mêmes conditions en présence des produits d'une réaction précédente. Les valeurs des périodes d'induction ne sont qu'approximatives.

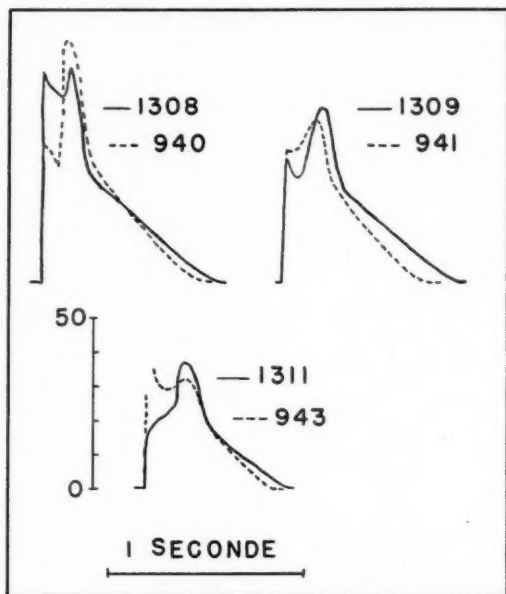


FIG. 5. Influence de l'acétaldéhyde sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène à 215°C. Pour les oscillogrammes en traits pointillés, la moitié de l'éther a été remplacée par de l'acétaldéhyde. Les données apparaissent dans le Tableau II.

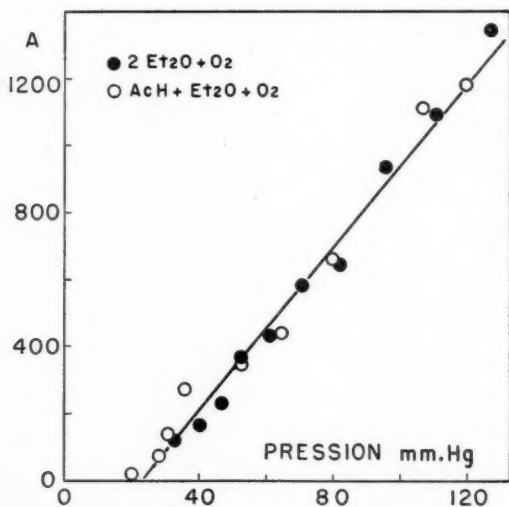


FIG. 6. Emissions intégrales A de flammes froides à 215°C., à partir de mélanges contenant 33% d'oxygène, avec soit 66% d'éther, soit 33% d'éther et 33% d'acétaldéhyde.

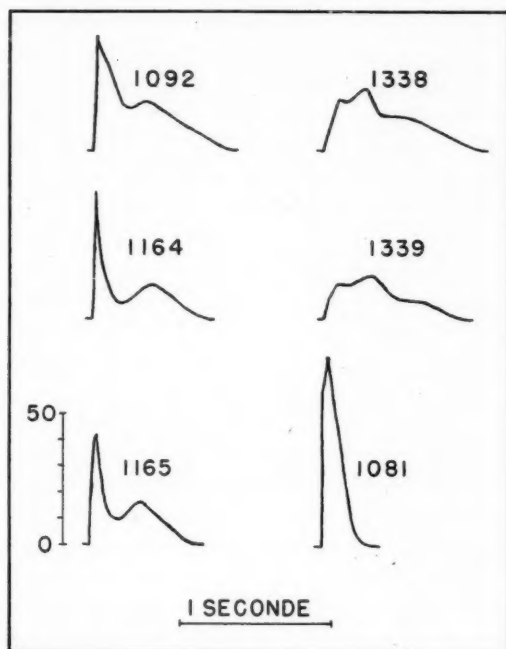


FIG. 7. Influence des produits de la réaction.

1338-1339. Les oscillogrammes obtenus en présence des produits de la réaction sont comparés à ceux que l'on obtient sans produits.

1081. Le mélange a été chauffé 20 min. à 166°C. avant d'être introduit dans la chambre à réaction à 215°C.

Un mélange qui avait été maintenu durant 20 min. à 166°C., température à laquelle il n'y a pas de flamme froide, et introduit ensuite dans le récipient à 215°C., a donné la flamme (1081) de la Figure 7, au lieu de la flamme (1165) qui aurait eu lieu dans les conditions normales. On trouvera, au Tableau III, quelques données concernant ces flammes.

TABLEAU III

INFLUENCE DES PRODUITS D'UNE RÉACTION PRÉCÉDENTE À LA PRESSION RÉSIDUELLE P_r , SUR LES FLAMMES FROIDES DE MÉLANGES ÉQUIMOLÉCULAIRES D'ÉTHÉR ET D'OXYGÈNE À 215°C. MÊMES SYMBOLES QU'ÀUX TABLEAUX I ET II

Expérience No.	P_{Et}	P_{O_2}	Produits	A , mm. ²	τ , sec.	P_r , %
	mm. Hg					
1338	32	32	10	620	2	13
1092	32	33	0	800	0.1	0
1339	25	25	7	500	2	12
1164	24	24	0	420	0.1	0
1342	30	30	23	—	20	27
1340	15	15	10	—	300	25
1341	25	25	26	—	300	25
1081	26	26	0	520	0.1	?
1165	26.5	26.5	0	525	0.1	0

Discussion

La complexité des effets constatés montre qu'il serait prématuré d'étendre les conclusions à des conditions trop éloignées de celles auxquelles on s'en est tenu dans cette étude préliminaire: mélanges équimoléculaires à 215°C. En particulier, les effets opposés de l'azote à 10% et à 50% peuvent être rapprochés des observations de Chamberlain et Walsh (1) sur le renversement de l'influence de ce gaz quand on dépasse certaines valeurs de la pression et de la température.

En ce qui concerne les gaz neutres, il semble que l'on puisse leur attribuer trois actions principales, susceptibles de produire dans certaines conditions des effets opposés.

(a) Inhibition du rendement lumineux. Il est possible que cette action s'exerce sur un processus thermique, puisque les pouvoirs inhibiteurs de ces gaz sont, à la précision des mesures près, parallèles à leurs chaleurs moléculaires: H_2 , N_2 , CO_2 , H_2O , (4.4, 4.9, 5.9, 6.6 cal. mole⁻¹ degré⁻¹). Spence et Townend (5) ont observé un effet du même ordre sur le déplacement de la limite d'inflammation.

(b) Exaltation du rendement lumineux aux forts pourcentages (52% N_2), vraisemblablement par protection d'un processus en chaînes qui serait inhibé par la paroi ou par un produit de la réaction. Le coefficient de température de l'émission intégrale étant légèrement négatif (3), une diminution de l'auto-échauffement par addition d'un diluant produirait un effet du même signe, mais probablement trop faible. De plus, cet effet serait plus considérable pour CO_2 que pour N_2 , ce qui est contraire à nos observations.

(c) Prolongement de la durée (52% N_2 et 33% CO_2). Cet effet est semblable à celui que l'on obtient en augmentant le diamètre du récipient (4), ce qui équivaut à diminuer l'influence relative des parois. Comme la durée est aussi prolongée par un abaissement de la température (3), on pourrait attribuer ce ralentissement à une diminution de l'autoéchauffement temporaire du mélange, dont la capacité calorifique est accrue par l'addition d'un diluant. Mais s'il en était ainsi, l'agrandissement du récipient, avec réduction concomitante du rapport surface/volume, tendrait à favoriser l'auto-échauffement et à abréger la durée, ce qui est contraire à nos résultats. Il est plus probable qu'une réaction en chaînes catalysée par la paroi, et correspondant peut-être à une étape obscure qui sépare les deux crêtes (6), est ralentie par l'addition d'un gaz neutre.

La formaldéhyde diminue le rendement lumineux et ralentit toutes les étapes de la réaction, y compris la période d'induction. En particulier la première crête, généralement aiguë, est arrondie et amortie. Comme cette substance est produite au cours d'une flamme froide normale, elle doit aussi y exercer les mêmes effets inhibiteurs. Si on lui attribue l'amortissement des crêtes qui suivent la première, on peut conclure qu'elle est absente durant la période d'induction, qu'elle aurait pour effet de prolonger, et aussi durant la majeure

partie de la crête initiale, qui est atteinte très rapidement et reste aiguë dans les flammes normales. Il est remarquable qu'aux très faibles pourcentages d'éther, la flamme froide présente une série de crêtes très aiguës (3), probablement parce que la formaldéhyde n'atteint pas une concentration suffisante. Puisque ces conditions sont justement celles dans lesquelles apparaissent les pulsations les plus nettes, il est difficile d'attribuer ces pulsations à l'influence inhibitrice de la formaldéhyde.

L'acétaldéhyde, bien qu'elle impose à la flamme de l'éther une période d'induction appréciable, contribue à l'émission lumineuse dans une mesure telle que sa substitution partielle à l'éther, molécule pour molécule, passe pour ainsi dire inaperçue. Cette égalité des rendements lumineux porte à croire qu'une molécule d'éther, malgré ses quatre atomes de carbone, ne donne naissance qu'à une molécule d'acétaldéhyde.

En présence des produits de la réaction, on doit s'attendre à retrouver les effets des aldéhydes. On observe la période d'induction prévue, mais il est remarquable que les pulsations soient amorties comme en présence de formaldéhyde tandis que l'émission intégrale reste intacte comme en présence d'acétaldéhyde. Il se peut que la formaldéhyde présente ralentisse la formation de l'acétaldéhyde sans altérer la quantité de ce produit, dont découle l'espèce responsable de l'émission lumineuse.

La flamme intense et brève obtenue à 215°C. après chauffage prolongé à 166°C. doit probablement son caractère à ce que l'étape de la formation des peroxydes est complètement franchie avant le début de la flamme, tandis qu'elle se poursuit ou se répète au cours d'une flamme ordinaire.

Remerciements

Ce travail a été subventionné par le Defence Research Board, auquel nous adressons nos plus vifs remerciements.

Summary

The influence of hydrogen, nitrogen, water vapor, carbon dioxide, formaldehyde, and acetaldehyde on the cool flame of ether has been studied, using the previously described photoelectric method (4). The first gases act like diluents. Formaldehyde is an inhibitor. Replacing a certain amount of ether by acetaldehyde or adding the products of a previous reaction makes the induction period longer but does not change the total amount of light emitted.

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THE RHEOLOGICAL PROPERTIES OF SOME SOAP-OIL SYSTEMS¹

BY G. B. MOSES AND I. E. PUDDINGTON

Abstract

The flow properties of dispersions of sodium, lithium, and aluminum soaps in hydrocarbon oils have been measured over a range of temperature, concentration, and rate of shear using an extrusion plastometer. The variations of residual viscosity and coefficient of thixotropy, with temperature, are similar for all of the soaps. Abrupt changes occur at temperatures that are characteristic of the individual soaps. The variation of thixotropy with concentration is in accord with theoretical predictions, and axial ratios of the solid phase particles, calculated from viscosity data, are in agreement with observed values.

Introduction

Dispersions of soaps, frequently of fairly high chemical purity, in suitable liquid hydrocarbons are commonly used as lubricating greases. One of the most interesting properties of these two phase systems is their behavior under shearing stress. A previous paper (4) discussed calcium soaps in this connection and the present communication is concerned with the properties of dispersions of other soaps.

Experimental

The experimental procedure was similar to that used previously (4). Dispersions were extruded through a metal capillary 2.611 cm. long, with a radius of 0.0368 cm., using compressed nitrogen as a source of variable pressure. A period of one hour was allowed at each temperature for thermal equilibrium to be established before measurements were made. Apparent viscosities were calculated from the Poiseuille equation, and the mean rate of shear was taken as $\frac{4V}{\pi r^3 t}$ where the symbols have their usual meaning. This value of the rate of shear is open to question and $2V$ or $3V$ might be preferable to the $4V$ actually used in the expression. However, with thixotropic systems the conditions of shear in the capillary are not readily ascertained and as the coefficients of thixotropy are used comparatively the value chosen for the rate of shear is not critical.

Graphs relating apparent viscosity and reciprocal of the rate of shear were prepared for each soap concentration at each temperature. These showed linear relations in the high shear range, and from the linear portion of the curve and its extrapolation, the coefficient of thixotropy (θ) and the residual viscosity (η_0) of the system were found.

Different concentrations of soap were prepared by diluting a concentrated sample with the oil used in its preparation, with as gentle agitation as pos-

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sible, to give samples in which the soap particles remained substantially in their original condition. The soap concentrations were determined by exhaustive extraction with petroleum ether and by ashing. Densities of concentrated samples were determined dilatometrically and the values for the diluted samples were calculated from the degree of dilution.

The mean rates of shear used in the measurements varied from 1400 to 250,000 sec^{-1} and the temperatures varied from 35°C. up to temperatures where the dispersions showed sufficient separation to give results of poor reproducibility or where solution of the soap in the oil was sufficient to reduce the coefficient of thixotropy to a very low value.

Samples of commercial lubricating grease and the oils used during the work were supplied gratuitously by Imperial Oil Limited, to whom grateful acknowledgment is made.

Sodium Soaps

Dispersions of these soaps are quite stable to heat but have limited usefulness in the presence of moisture. A small amount of water of hydration has been considered essential for their formation (3) although good dispersions can be obtained under anhydrous conditions. It is possible to obtain the individual soap particles in a variety of axial ratios by suitable adjustments in the degree of unsaturation of the fatty acid used in the soap preparation, the type of hydrocarbon oil, and the procedure used in preparing the dispersions (1). When heated, the whole character of these systems changes at a temperature which is characteristic of the soap. When this happens the rheological properties also undergo very substantial changes.

In the present work two types of preparations were used. One was a commercial grease containing 19.7% of soap dispersed in an oil of 335 S.U.S. at 100°F. and a viscosity index of 48. Several samples were prepared from this dispersion by dilution. In the second group of samples U.S.P. grade sodium soaps and the same oil as contained in the commercial sample were used. Five samples were prepared, all containing 15% of soap. Various degrees of unsaturation were obtained by mixing sodium stearate and oleate. The percentages of stearate contained in the various soaps were 100, 75, 50, 25, and 0. The dispersions were made by suspending the dry soap in the oil, heating the mixture to about 120°C., and passing it through the colloid mill. Previous experience showed that this procedure produces dispersions of good uniformity (1).

The length of the soap particles in several of the samples was altered by subjecting the sample to various rates of shear at about room temperature. Samples of the diluted commercial grease were passed through a colloid mill (mean rate of shear about 700,000 sec^{-1}) and allowed to stand for 24 hr. before taking measurements. Part of the sample containing 15% of pure sodium stearate was passed three times through a capillary at a mean rate of shear of 2000 sec^{-1} and a second portion was passed through the colloid mill. This procedure should produce three fiber lengths in identical concentration.

The results of the viscometric measurements made on these various samples are summarized in Tables I and II where values of the residual viscosities in poises and coefficients of thixotropy in dynes per cm.² at the different temperatures are recorded. The symbols "*l*", "*m*", and "*s*", are used here to indicate samples that are in their original state, samples lightly sheared, and samples highly sheared by passage through the colloid mill, respectively.

TABLE I
RESIDUAL VISCOSITIES AND COEFFICIENTS OF THIXOTROPY FOR
DISPERSIONS OF SODIUM SOAPS (COMMERCIAL)

Conc. Vol. %	Temperature, °C.												
	35°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°
19.7 (<i>l</i>) θ	19820	11700	7480	5220	3790	3320	3830	7920	8150	8270	7880	7250	5900
η_0	7.40	4.20	2.75	1.75	1.20	0.75	0.45	0.25	0.97	1.69	1.22	0.45	0.15
19.7 (<i>s</i>) θ	7300	5350	4350	3600	3000	2900	3300	4900	6500	6950	6850	6300	5600
η_0	2.90	1.35	0.87	0.57	0.43	0.32	0.25	0.20	0.20	0.41	0.50	0.45	0.30
14 (<i>l</i>) θ	9370	5320	2850	1700	1250	970	1220	2330	3800	3800	3790	2900	1330
η_0	2.25	1.19	0.84	0.59	0.43	0.31	0.24	0.19	0.21	0.27	0.25	0.21	0.17
14 (<i>s</i>) θ	2830	1820	1580	1390	1340	1320	1590	1730	1760	1800	1720	1600	1350
η_0	1.91	0.97	0.62	0.45	0.29	0.26	0.41	0.54	0.60	0.83	0.90	0.79	0.43
10 (<i>l</i>) θ	6850	3600	1800	800	400	250	500	1100	2400	3200	3150	3270	900
η_0	1.56	0.78	0.53	0.37	0.28	0.21	0.16	0.14	0.14	0.15	0.13	0.11	0.09
10 (<i>s</i>) θ	1460	970	810	480	450	430	800	980	1010	1110	1100	1050	1000
η_0	1.40	0.62	0.42	0.34	0.21	0.17	0.18	0.16	0.22	0.36	0.33	0.23	0.11

NOTE: η_0 = poises.

θ = dynes/cm.²

TABLE II
RESIDUAL VISCOSITIES AND COEFFICIENTS OF THIXOTROPY FOR
DISPERSIONS OF SODIUM SOAPS (PURE)*

Ratio of stearate to oleate	Temperature, °C.												
	35°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°
100-0 (<i>l</i>) θ	45200	28700	21500	15900	10300	6900	4800	3700	3300	4500	7600	5500	2300
η_0	3.30	1.60	1.04	0.70	0.62	0.55	0.38	0.27	0.30	0.30	0.30	0.32	0.36
100-0 (<i>m</i>) θ	19800	12800	8800	5800	3400	1900	1800	1700	1000	2600	6000	4100	1200
η_0	3.00	1.41	0.93	0.66	0.46	0.34	0.25	0.21	0.21	0.21	0.22	0.22	0.26
100-0 (<i>s</i>) θ	11780	7750	5350	3350	2000	1170	1120	960	1050	2130	5350	3310	730
η_0	1.91	1.03	0.73	0.55	0.39	0.28	0.19	0.15	0.13	0.14	0.17	0.19	0.24
75-25 (<i>l</i>) θ	45300	34100	29400	23700	20300	21200	24000	45300	22800	16200	12400	9400	5600
η_0	5.0	3.45	2.8	2.3	1.7	1.3	0.9	5.2	0.6	0.7	0.6	0.5	0.3
50-50 (<i>l</i>) θ	59200	48000	43800	40000	37500	48500	39400	29200	22200	15900			
η_0	3.25	2.28	1.71	1.18	0.84	0.65	0.54	0.44	0.35	0.40			
25-75 (<i>l</i>) θ	71200	41100	31300	38100	43700	48700	38400	31100	24600	19700	15300	8750	
η_0	3.00	2.40	2.00	1.54	1.20	0.85	0.85	0.81	0.75	0.65	0.50	0.30	
0-100 (<i>l</i>) θ	64100	43600	34200	31300	30100	30300	33400	25500	18500	13400			
η_0	3.65	2.80	2.30	1.93	1.60	1.35	0.95	0.72	0.50	0.45			

* Concentration of soap 15% by volume in each case.

The general behavior of the sodium soap dispersions is similar to that of calcium soap. When examined over a range of temperatures both coefficient of thixotropy and residual viscosity have rather high values at low temperatures and these fall rapidly to a minimum as the temperature is increased. This is followed by a sharp maximum in these quantities with further temperature increases. At higher temperatures the values again fall off as the soap goes into solution. This behavior is shown in Fig. 1, which shows a plot of θ vs. temperature for the commercial grease. The minimum and maximum shown here at 100° and 130°C., respectively, correspond to similar phenomena with

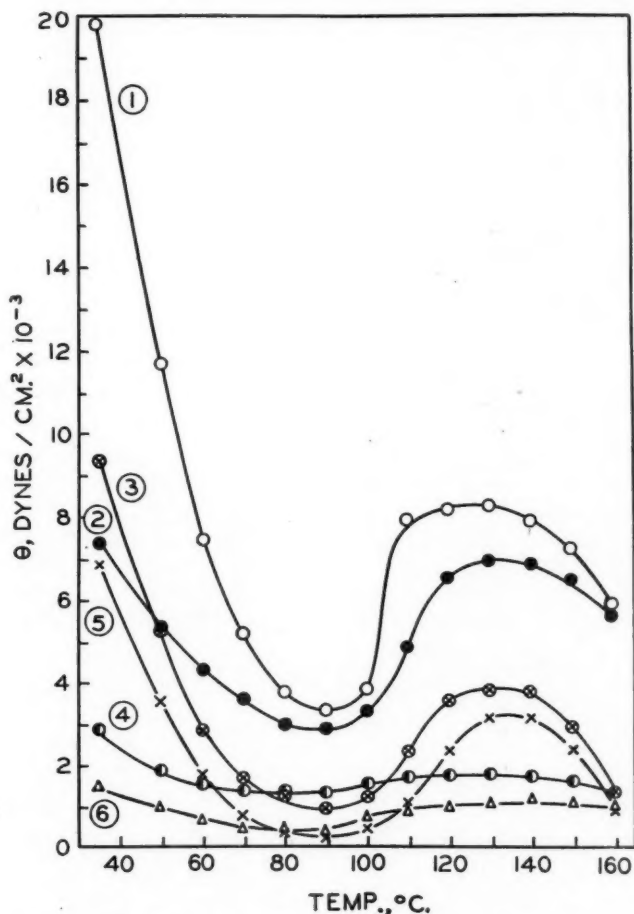


FIG. 1. Change in the coefficient of thixotropy with temperature at different concentrations and fiber lengths for dispersions of commercial sodium soaps. The graphs represent: (1) 19.7% soap, (l); (2) 19.7% soap, (s); (3) 14% soap, (l); (4) 14% soap, (s); (5) 10% soap, (l); (6) 10% soap, (s).

calcium soap greases at 50° and 65°C. That the degree of unsaturation of the soap has considerable influence on the temperature at which the minimum and maximum occur is shown in Fig. 2 where the soap contains various ratios of oleate to stearate. Here the temperature of minimum thixotropy itself goes through a minimum as one passes from pure sodium oleate to pure sodium stearate. This minimum occurs at a temperature of 60°C. and a molecular ratio of 3 to 1 of oleate to stearate.

It is also noteworthy that mixtures of these two molecules produce higher maxima than either of the pure soaps alone. Finally, a 60°C. spread is found

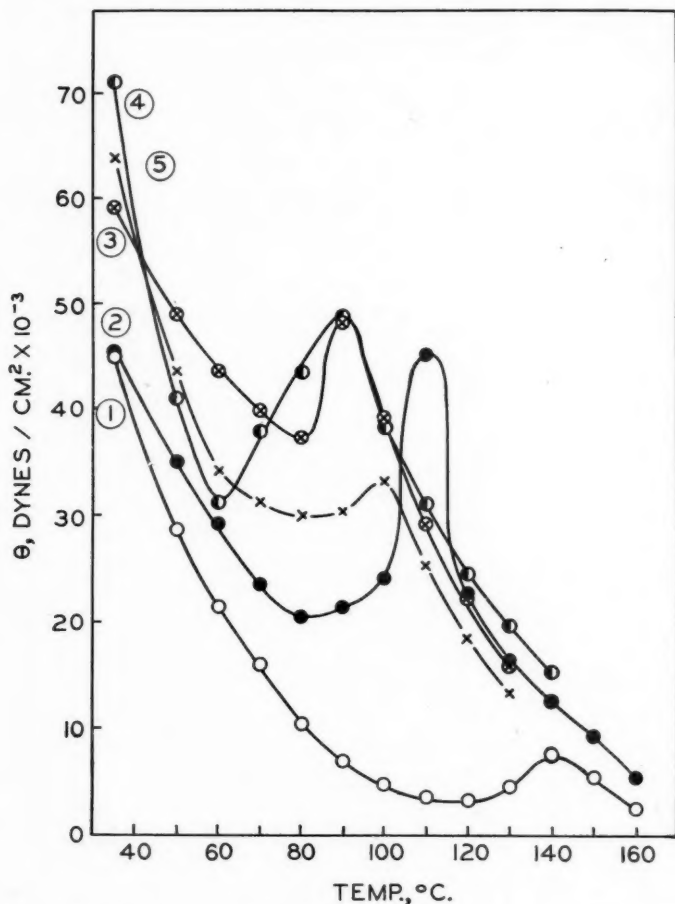


FIG. 2. Change in the coefficient of thixotropy with temperature for dispersions of mixtures of pure sodium stearate-sodium oleate soaps. The graphs represent: (1) 100% sodium stearate; (2) 75:25% sodium stearate-sodium oleate; (3) 50:50% sodium stearate-sodium oleate; (4) 25:75% sodium stearate-sodium oleate; (5) 100% sodium oleate.

in the position of the minimum coefficient of thixotropy as one passes through the composition range. This is of considerable practical importance since, normally, it is not advisable to use grease at temperatures in excess of this minimum. This means that the useful temperature range of the grease may be considerably extended by suitable selection of the soap stocks.

While the temperature at which the minimum and maximum in the coefficient of thixotropy depends only on the soap molecule, the difference between the maximum and minimum values of the coefficient are influenced considerably by the shape of the soap particles. This is shown in Fig. 1 where three concentrations of soap are shown. One group was passed through a colloid mill and the other is in its original form. From microscopic examination, shearing in the cold appears to shorten the fibers only. Since the coefficient of thixotropy depends on the mutual interference of the particles, it is obvious that the effective volume occupied by the longer fibers is more important than the increased number of individual particles produced by the shearing process.

The much smaller temperature coefficient of thixotropy shown in the case of the shorter particles is also of interest. This may be due to the increased flexibility of the longer fibers at the higher temperatures which would make easier separation of mechanical entanglements possible, while the force required to separate a physical contact would remain virtually constant as the temperature is increased. Identical behavior was observed when pure sodium stearate dispersions were treated in the same way.

The curve for residual viscosity vs. temperature is similar in shape to the thixotropy-temperature relation. The initial drop is to be expected since over this temperature range the soap remains comparatively inert and the behavior is similar to that of the oil alone. As the soap absorbs oil at the higher temperatures the liquid phase becomes depleted and the effective soap concentration increases, causing a viscosity increase. A minimum thus appears in the viscosity curve. Eventually, on further increases in temperature, the soap goes into solution in the oil and when this process proceeds to a greater extent than solution of the oil in the soap, a maximum appears in the viscosity curve. With further temperature increases the viscosity of the system falls rapidly.

Lithium Soaps

Dispersions of lithium soaps in oils have recently become of interest on account of their stability at high temperatures and in the presence of moisture. They are usually prepared from a fairly pure grade of lithium stearate by heating the suspension formed in the cold to a temperature in excess of complete solubility (about 200°C.). The soap crystals formed on cooling are considerably smaller than those of sodium stearate. The rheological properties of the dispersions are qualitatively similar to those of sodium and calcium soaps. The only significant difference is the higher temperatures at which the viscosity minimum and maximum occur.

Experimental data are presented in Table III and in Figs. 3 and 4. These were obtained from a commercial preparation suitably diluted to give the various concentrations. The letters "l" and "s" used in Table III indicate original samples and those passed through the colloid mill, respectively. It is of interest that shearing produced considerably less reduction in thixotropy in the case of lithium stearate dispersions than with sodium stearate of similar concentration. This is apparently due to the greater resistance of the smaller crystals to mechanical breakup by the shearing stress.

TABLE III
RESIDUAL VISCOSITIES AND COEFFICIENTS OF THIXOTROPY FOR
DISPERSIONS OF LITHIUM SOAPS

Conc. Vol. %	Temperature, °C.														
	35°	50°	65°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°	190°
26.9 (l) θ	28770	18860	14010	11100	10110	6930	5980	5450	5480	4810	3270	3170	4320	3440	
η_0	6.9	3.1	1.5	0.9	0.6	0.7	0.7	0.7	0.7	0.7	0.9	0.5	0.6	0.6	
26.9 (s) θ	17590	15010	10000	8020	6920	5780	5010	4670	4550	3800	2920	2690	3410	2940	
η_0	5.15	2.60	1.35	0.84	0.71	0.63	0.62	0.63	0.67	0.74	0.86	1.12	1.34	1.46	
18 (l) θ	12300	8950	7010	5680	5250	4200	3990	3700	3800	3530	2950	3820	8650	5200	1700
η_0	1.15	0.65	0.47	0.38	0.19	0.16	0.15	0.13	0.14	0.13	0.10	0.27	0.65	0.95	0.64
18 (s) θ	6470	6010	5400	4710	3970	3260	3040	2860	2920	2580	2360	2440	3750	3910	2870
η_0	1.36	0.70	0.44	0.28	0.20	0.16	0.15	0.16	0.18	0.24	0.31	0.50	0.90	1.36	0.90
9 (l) θ	3470	3123	2847	2793	2320	2050	1975	1890	1712	1660	1294	1090	1800	1780	3460
η_0	0.80	0.50	0.30	0.20	0.15	0.12	0.09	0.08	0.06	0.06	0.15	0.49	0.52	0.67	0.20
9 (s) θ	2940	2400	2000	1560	1420	1310	1280	1230	1260	1210	950	690	930	1020	970
η_0	0.56	0.26	0.18	0.13	0.10	0.09	0.07	0.06	0.07	0.08	0.10	0.13	0.30	0.41	0.15

Aluminum Soaps

For comparative purposes, results from a single concentration (6%) of pure aluminum distearate in an oil of 893 S.U.S. 100°F. viscosity are shown in Figs. 5 and 6. This dispersion was prepared in the same way as those of lithium stearate. In the case of aluminum soaps the crystals are too small to be resolved microscopically.

The general shape of the residual viscosity and thixotropy curves is similar to those of other soaps. Obviously the usefulness of these dispersions as lubricants is restricted to low temperatures.

Discussion

The explanation advanced for the shape of the residual viscosity vs. temperature curve for sodium stearate is equally applicable to the other soaps. The similar behavior of the coefficient of thixotropy at the lower temperatures is not so readily explained, however. In the particular case of dispersions of calcium soaps where an excess of a third phase (water) is present, the agglomeration of the solid phase which is responsible for the degree of thixotropy, may

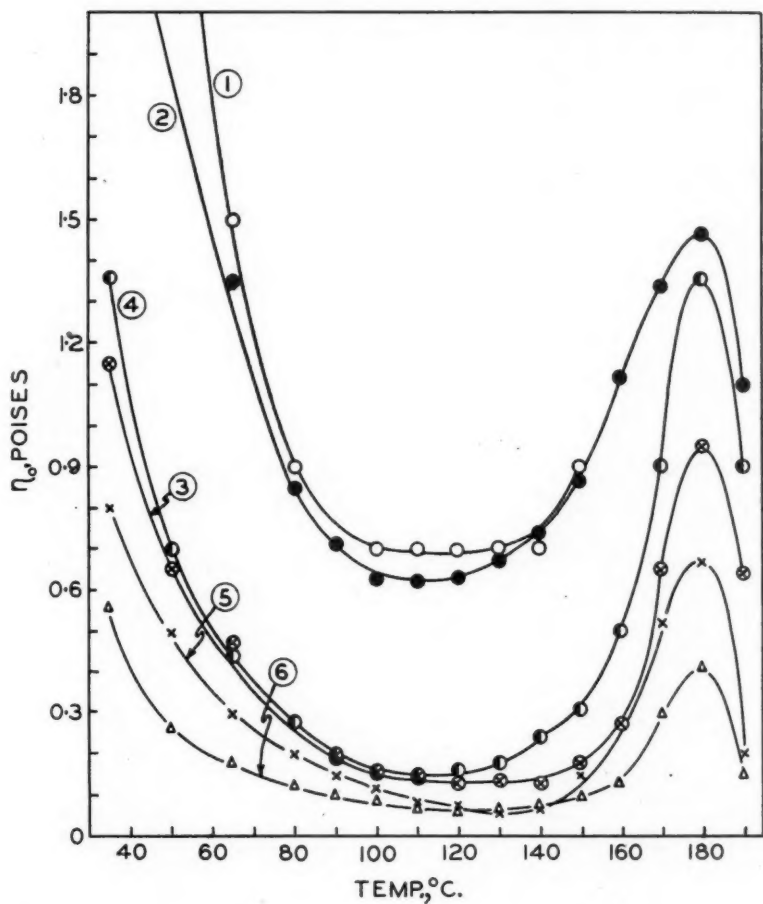


FIG. 3. Change in residual viscosity with temperature at different concentrations and fiber lengths for dispersions of lithium soaps. The graphs represent: (1) 26.9% soap (l); (2) 26.9% soap, (s); (3) 18% soap, (l); (4) 18% soap, (s); (5) 9% soap, (l); (6) 9% soap, (s).

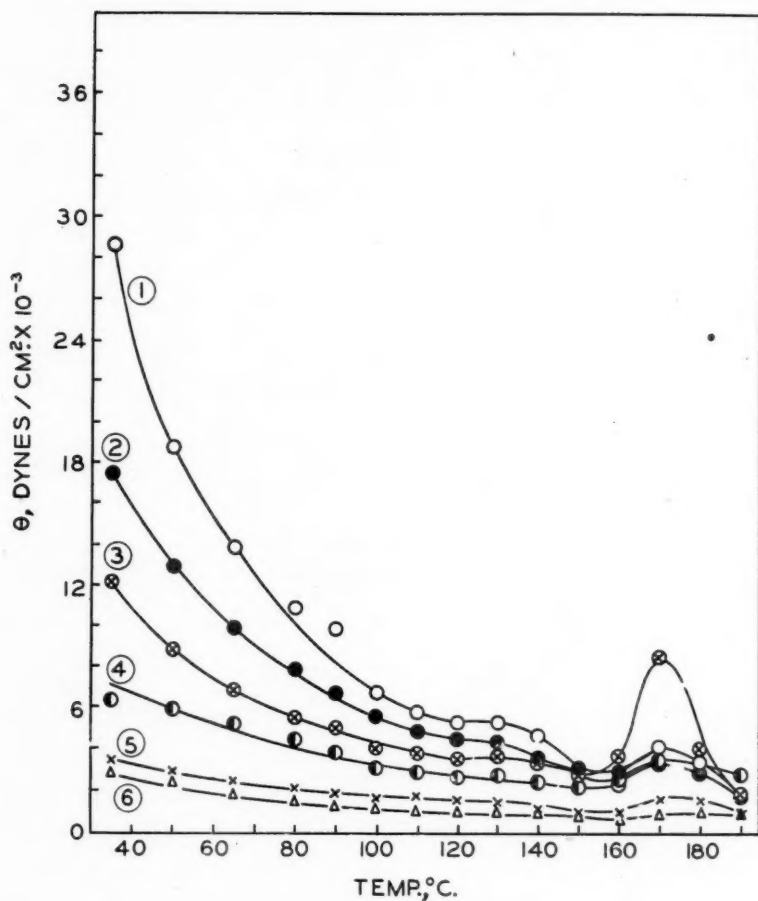


FIG. 4. Change in the coefficient of thixotropy with temperature at different concentrations and fiber lengths for dispersions of lithium soaps. The graphs represent: (1) 26.9% soap (l); (2) 26.9% soap (s); (3) 18% soap (l); (4) 18% soap (s); (5) 9% soap (l); (6) 9% soap (s).

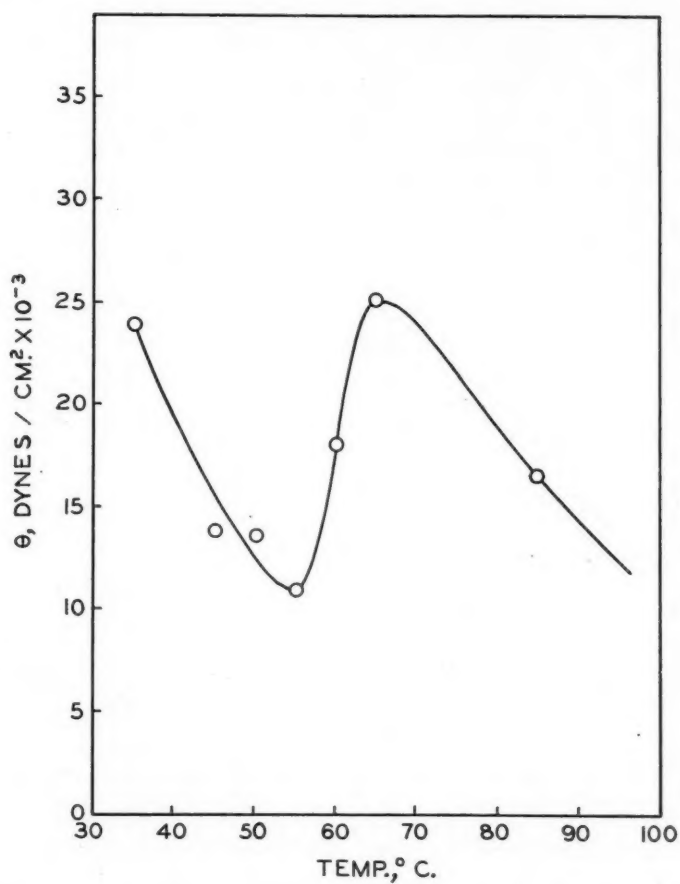


FIG. 5. Change in coefficient of thixotropy with temperature for dispersion of pure aluminum stearate.

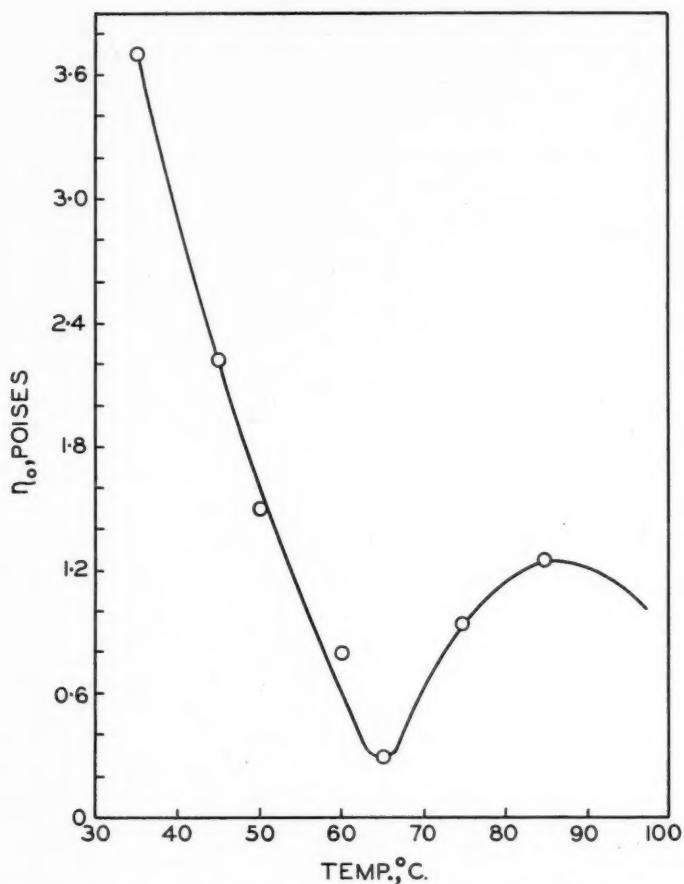


FIG. 6. Change in residual viscosity with temperature for dispersion of pure aluminum stearate.

be due to the interfacial surface tension of the two liquids (2). This would be expected to become less with increase in temperature with a consequent drop in thixotropy. Such can not be the case, however, with the three systems under consideration here, since they are substantially anhydrous. Mechanical entanglement of the particles with the consequent formation of strong links seems to be a more likely explanation. In this case the reduction in thixotropy at the higher temperatures is possibly due to greater flexibility of the fibers as the temperature is increased, which allows for much easier breakdown of agglomerates. This hypothesis is supported by the fact that shear sufficiently high to reduce the length of the particles also produces a strong reduction in the degree of thixotropy and also a marked lowering in the temperature coefficient of

thixotropy. Shorter particles would certainly contribute less to mechanical entanglement but would not reduce the number of interparticle contacts. Were the adhesion due to interparticle friction or interfacial tension, the temperature sensitivity to shape should be less pronounced.

The increase in thixotropy following the initial reduction observed with all the soaps is undoubtedly due to swelling of the soap crystals. The tacky surfaces produced by the swelling causes increased agglomeration which finally passes through a maximum as the soap particles go into solution.

Finally the increasing temperatures of the point of minimum thixotropy and viscosity as one passes from aluminum through calcium, sodium, and lithium stearates appears to be due to the influence of the metallic ion forming the soap and is in the direction of increased electropositivity.

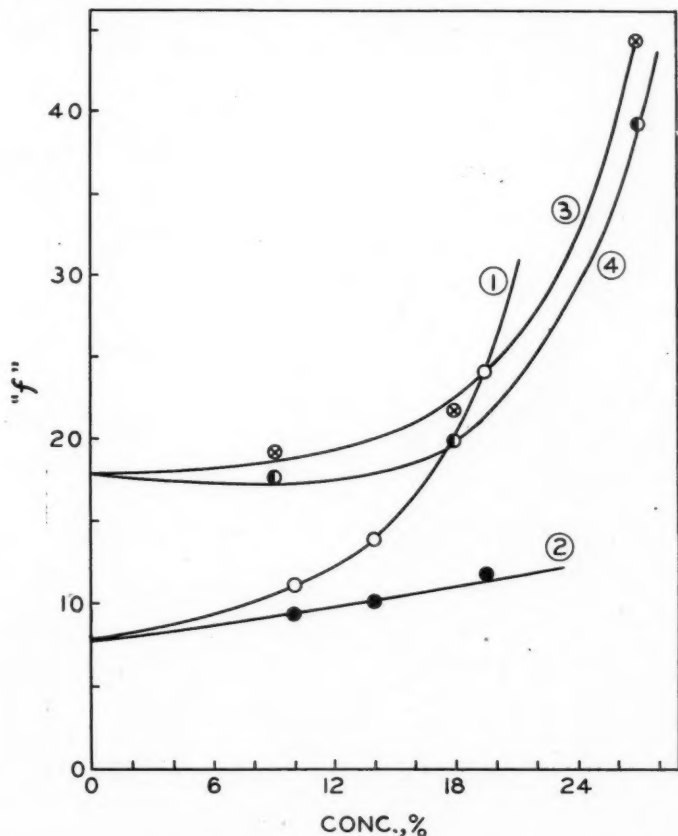


FIG. 7. Relationship of fiber axial ratio to concentration for some sodium and lithium soap dispersions. The graphs represent: (1) 19.7% commercial sodium soap (l); (2) 19.7% commercial sodium soap (s); (3) 26.9% lithium soap (l); (4) 26.9% lithium soap (s).

Attempts have been made previously to get information on the shape of the individual particles of the solid phase by applying the Kuhn equation relating viscosity to volume concentration and shape factor, to the residual viscosity data (4, 5). Results from this work have also been used in this connection with some success. Lithium soap particles gave an extrapolated shape factor of 15 at zero concentration. Sodium soaps at 15% concentration gave a value of 17 for 100% stearate which increased to 23 at 100% oleate, an expected difference. Passage of a sodium stearate - oleate grease through the colloid mill had virtually no effect on the shape factor after extrapolation to zero concentration. The apparent shape at higher concentrations, however, was quite different. Microscopic examination showed progressively less difference in the sheared and unsheared samples as one passed from the higher to the lower concentrations of soap. This would indicate that damage to the soap fibers at a definite

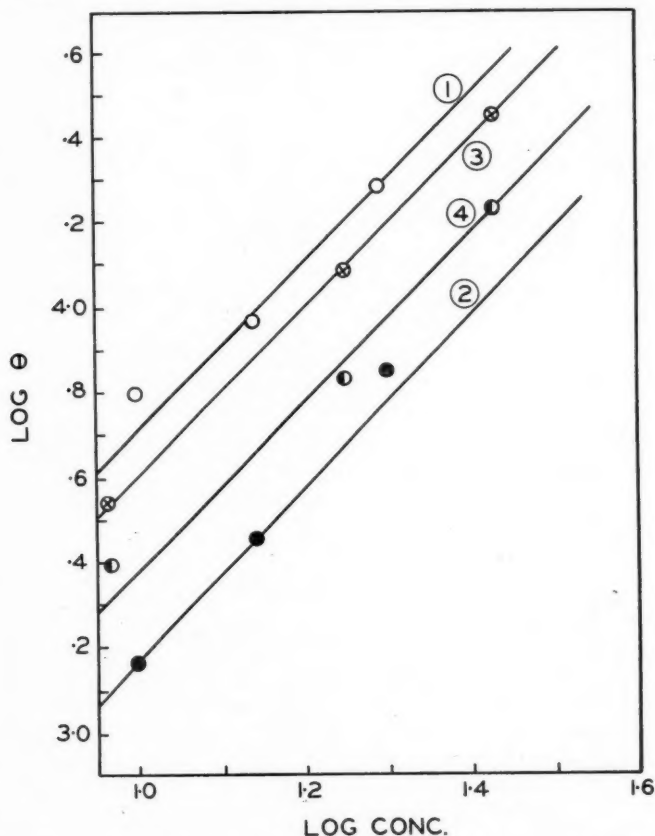


FIG. 8. Change in coefficient of thixotropy with concentration. The graphs represent: (1) 19.7% commercial sodium soap (l); (2) 19.7% commercial sodium soap (s); (3) 26.9% lithium soap (l); (4) 26.9% lithium soap (s).

rate of shear is dependent on the soap concentration, and at low percentage of soap little disintegration of the soap particles occurs. A similar result was obtained with dispersions of lithium stearate. In this case, however, the damage even at high concentrations was slight, owing to the small size of the individual soap particles. These results are shown in Fig. 7. The values quoted above for axial ratios are in agreement with microscopic observations. The "f" values given were calculated from data at 35°C. The calculated axial ratios are substantially independent of temperature, however, below the minimum in the η_0 vs. temperature curve. At higher temperatures the values increase, indicating strong adhesion of the solid particles.

Theory predicts a slope of 2 when the logarithm of the coefficient of thixotropy is plotted against the logarithm of the concentration. The agreement between theoretical and experimental values for these soap systems is shown in Figure 8. All the curves have been drawn with a slope of 2 but a reasonably good fit with the experimental points has been obtained.

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REACTIONS IN DISSOCIATED WATER VAPOR¹

BY R. A. JONES AND C. A. WINKLER

Abstract

Water vapor dissociated by an electric discharge and passed into a cold trap yielded products which gave off oxygen at temperatures above -120°C . and at room temperature consisted of hydrogen peroxide and water. With products formed under given conditions, the amount of oxygen evolved with warming was proportional to the total amount of product and independent of the warming procedure. The evolution proceeded to completion at -78°C . Water was found at all trap temperatures between -78°C . and -195°C . Hydrogen peroxide was formed only if the trap temperature was below -120°C ., and oxygen was evolved only from products formed below -150°C . The yields of water, hydrogen peroxide, and evolved oxygen all increased with decreasing trap temperature. As the volume of reaction chambers inserted between the discharge tube and the trap was increased, the yield of hydrogen peroxide decreased continuously, while the yield of water at first decreased and then increased to a limiting value. Packing a given reaction chamber with glass wool drastically reduced the yield of hydrogen peroxide, but had little effect on the yield of water. Packing the trap itself had only a slight effect on the yields. The results are compared with those obtained by others with the H-O_2 system at low temperatures, and a mechanism is proposed to correlate the two systems.

Introduction

When water vapor at low pressures is subjected to the action of a glow discharge of moderate current strength, the primary decomposition products are hydrogen atoms and free hydroxyl radicals (11). If the water vapor is passed continuously through the discharge, the effluent gases have characteristic properties, not all of which can be due to atomic hydrogen alone (3, 7, 18). The possible presence of hydroxyl radicals in these gases has been a matter of controversy. Early workers (18, 7, 8) assumed their presence on the basis of apparently faulty spectroscopic evidence. Subsequently Bonhoeffer and Pearson (2) deduced from spectroscopic data that the hydroxyl radicals disappear so rapidly that no appreciable number could survive outside the discharge. This was contradicted by the results of Oldenberg and his coworkers, who showed with a more refined technique that the hydroxyl absorption spectrum persisted in the discharge tube for at least 0.4 second after the current was interrupted (10, 11, 12). Recently, the assumption has again been made that the water vapor discharge can serve as a source of hydroxyl radicals (9).

Several investigations have shown that the final products of the decomposition are hydrogen, oxygen, water, and hydrogen peroxide in proportions which depend upon experimental conditions, including temperature (4), pressure (16), surface (16), and the presence of catalysts (17). Several mechanisms have been proposed (2, 16, 19) to explain the formation of these final products from the hydrogen atoms and hydroxyl radicals formed initially in the dis-

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charge, but some of the suggestions were based on an incomplete knowledge of the over-all reaction. Rodebush has recently proposed a mechanism which postulated the existence in the active gases of a high concentration of hydroxyl radicals which disappear in the gas phase at ordinary temperatures by an over-all reaction $\text{OH} + \text{OH} \rightarrow \text{H}_2 + \text{O}_2$, while at very low temperatures they condense to hydrogen peroxide (14).

This paper reports further investigation of the manner in which the relative yields of the final products depend upon experimental conditions.

Experimental and Results

The apparatus was a conventional flow system (Fig. 1). De-aerated redistilled water was frozen in flask *A* and maintained at 0°C. in an ice-water bath. Water vapor diffused from this flask through the flowmeter chamber *B* and flow-rate control *C* into the discharge tube *D* (22 mm. I. D.). The electrodes were hollow aluminium cylinders (5 cm. \times 1.5 cm.) placed 104 cm. apart, while the entrance and exit tubes for water vapor were 89 cm. apart. The discharge tube was cooled by tap water flowing through jacket *E*. High voltage 60 cycle current was supplied to the discharge by a transformer, the output of which could be controlled by a variable transformer in the primary circuit. In all experiments the discharge current was 200 ma. and the discharge potential 1250 v.

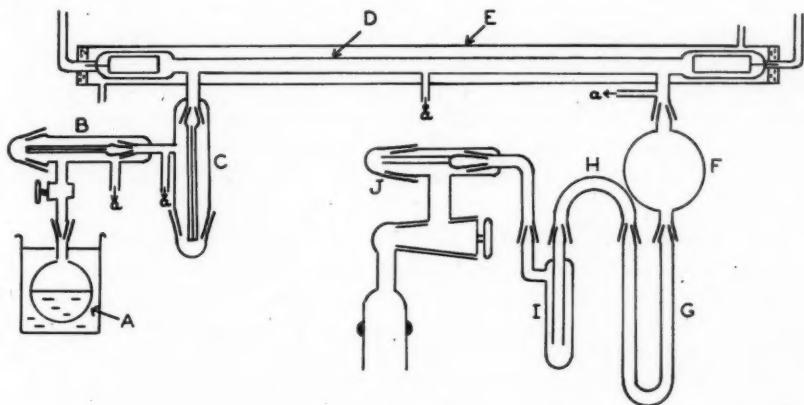


FIG. 1. Diagram of apparatus.

From the discharge tube the dissociated water vapor flowed through a short exit tube into reaction chamber *F* and thence into a cold trap *G*. Products not condensed in *G* passed through the connection *H* into a second trap *I* (included to prevent mercury vapor reaching *G* from the diffusion pump) and thence through a second flow-rate control *J* to the pumping system. This consisted of a high capacity three-stage mercury diffusion pump backed by a Welch "Duo-Seal" mechanical pump.

The various parts of the reaction chamber and trap assembly were connected by ground glass joints sealed with apiezon "M" grease. This arrangement permitted the insertion of different reaction chambers at *F*, and allowed trap *G* to be detached for product analysis.

By proper choice of flow-restricting tubes in chambers *B*, *C*, and *J*, the system could be operated, within limits, with any desired pressure in the discharge. In all experiments the water input was 15.27 millimoles (mM.) per hour and *J* was adjusted so that the pressure at the mid-point of the discharge tube was 0.1 mm. This procedure ensured that conditions in the discharge were constant for all experiments, regardless of the conditions to which the dissociated water vapor was subjected after leaving the discharge. Gas pressures were measured at points *a* in Fig. 1 by MacLeod gauges kept at 55°C. to prevent condensation of water vapor.

In most experiments, products were collected over a two hour period and the system was filled with dry nitrogen before detaching trap *G* for product analysis.

Gas Evolution from Condensed Product

In a typical experiment in which trap *G* was attached directly to the discharge tube and cooled with liquid nitrogen, the condensed product was obtained as a transparent glassy layer. When the trap was allowed to warm up, this glassy material became white and crystalline, with crystals growing out in rays from a few nuclei. As warming continued, the product melted to give a solution of hydrogen peroxide in water. Violent foaming occurred as the product melted, to produce a gas which was shown by density determination, combustion analysis, and treatment with potassium iodide solution to be oxygen containing about 0.4 mole % of ozone. No measurable amount of hydrogen was found.

In one experiment the trap, containing the product collected during two hours at -195°C., was connected to a manometer. After evacuation, the liquid nitrogen was replaced by isopentane cooled to -150°C. in a Dewar vessel, and the isopentane allowed to warm up slowly, with continuous stirring, while measurements of temperature and gas pressure were made. No oxygen was evolved until the temperature had risen to about -120°C. (Fig. 2). Thereafter the rate of evolution increased rapidly to a value which remained practically constant until evolution ceased. (For convenience, oxygen obtained by warming the cold trap will be designated as evolved oxygen.)

Several experiments were made to investigate the influence of warming procedure upon oxygen evolution. In parallel experiments, products collected in two hours at -195°C. were warmed to room temperature (1) abruptly, by immersing the trap in a water bath, (2) in two stages, by immersion in dry ice - acetone slurry followed by immersion in a water bath, and (3) in five stages, by successive immersion in baths at -78°C., -59°C., -46°C., 0°C.,

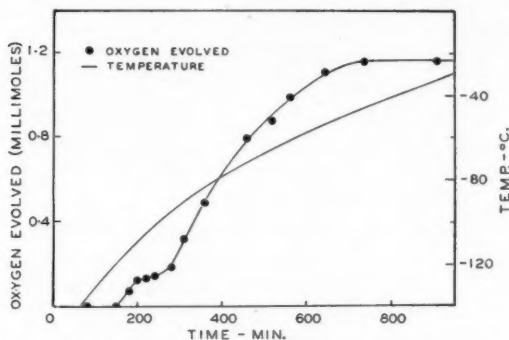


FIG. 2. Relation between oxygen evolved and time, with increasing temperature.

and room temperature. In all cases the final total amount of oxygen evolved was substantially the same as that obtained by gradual warming. Other experiments, made under identical conditions but for different lengths of time, so that different total amounts of product were obtained, showed that the yields of evolved oxygen, of hydrogen peroxide, and of water, were all directly proportional to the duration of the experiment.

In a further experiment on oxygen evolution, the cold product collected in four hours at -195°C . was warmed to -78°C . and maintained at that temperature for 24 hr. The results are shown in Fig. 3, in which the amount of oxygen evolved is plotted against time (Curve I) and reciprocal time (Curve II). A reasonable extrapolation of curve II to infinite time gives a value of 2.4 mM. for the amount ultimately evolved at -78°C ., i.e. the same as the quantity evolved from comparable amounts of product warmed to room temperature. At the end of the experiment the product (at -78°C .) had become white and crystalline.

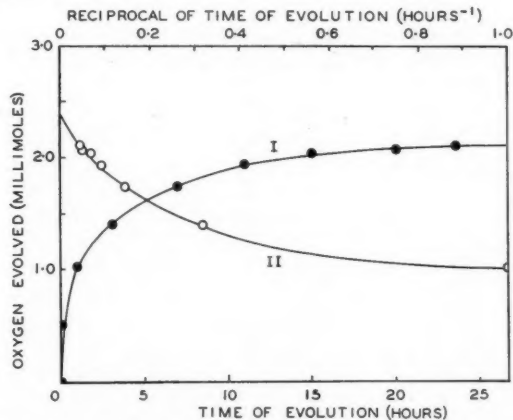


FIG. 3. Relation between oxygen evolved and time at -78°C .

Influence of Trapping Temperature

Earlier work (16, 14) has shown that both water and hydrogen peroxide are obtained at liquid air temperatures but only water is obtained at -78°C . In the present study, product yields were determined as a function of trapping temperature over the intervening range. The trap was attached directly to the discharge tube and was immersed in a vigorously stirred bath of propane or isopentane, which was maintained within 0.2°C . of the desired temperature by pouring small amounts of liquid nitrogen into a test tube suspended in the bath. After each experiment the product was warmed to 0°C ., and the evolved oxygen determined manometrically. The trap and residual contents were then weighed, and the hydrogen peroxide content determined by titration with standard potassium permanganate solution. The yield of water was calculated by difference. The amounts of oxygen and hydrogen formed during the experiment were also calculated by difference, from the known total input of water.

The results are given in Table I and Fig. 4. Noteworthy features are: (1) water was obtained at all temperatures; with increasing temperature the amount remained sensibly constant from -195°C . to about -160°C ., and then decreased to a lower limit, (2) no peroxide was obtained above -120°C . at which temperature a trace was formed. Below -120°C . the yield increased rapidly until at -195°C . it was 45% by weight of the water input; (3) measurable amounts of oxygen were evolved only from products collected below -150°C .; the yield increased almost linearly with decreasing trap temperature, and at -195°C . amounted to 8.4% of the oxygen input; (4) the amount of molecular oxygen formed during the experiment decreased very rapidly with decreasing temperature, so that at -195°C ., 95% of the oxygen input was collected in the trap.

TABLE I
VARIATION OF YIELDS WITH TRAP TEMPERATURE

Trap temperature ($^{\circ}\text{K}$.)	Yields: mM. per hour					
	H_2O_2	H_2O	Evolved O_2	O_2	H_2	H_2O formed at trap temperature*
193	0	3.84	0	5.72	11.43	0
173	0	4.00	0	5.64	11.27	0.16
153	0.01	4.36	0	5.45	10.90	0.52
138	0.20	5.11	0	4.88	9.96	1.27
123	0.47	5.81	0.03	4.24	8.99	1.91
113	0.97	5.98	0.09	3.59	8.32	1.96
103	1.50	5.93	0.21	2.97	7.84	1.67
93	2.88	5.92	0.41	1.57	6.83	1.26
78	3.74	5.90	0.64	0.31	5.63	0.78

* Assuming no water to be formed in trap at 193°K . and that, on warming, water and oxygen were formed in the molar ratio 2:1.

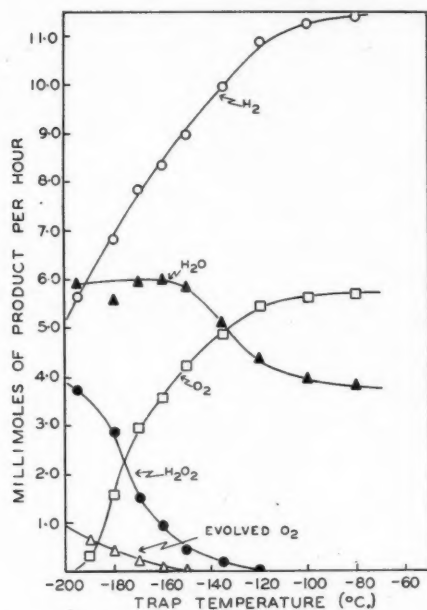


FIG. 4. Relations between product yields and trapping temperature.

Influence of Reaction Chamber

In another series of experiments the dissociated water vapor passed through a reaction chamber (*F* in Fig. 1) before entering the cold trap, so that reactions at room temperature proceeded for a time interval determined by the flow rate and the volume of the chamber. Experiments were made at trapping temperatures of $-195^{\circ}\text{C}.$ and $-78^{\circ}\text{C}.$ with four reaction chambers and also with the trap attached directly to the discharge tube (Table II and Fig. 5). Evolved oxygen was not determined. At $-78^{\circ}\text{C}.$, as expected, only water was

TABLE II

YIELDS WITH DIFFERENT REACTION CHAMBERS

	Chamber No. and shape				
	0	1 (Cylindrical)	2 (Spherical)	3 (Cylindrical)	4 (Spherical)
	Yields: mM. per hour				
Volume (ml.)	18	213	1027	1107	5512
Time of passage (sec.)	0.02	0.16	0.70	0.80	3.7
Volume: surface	—	0.088	2.0	0.44	3.6
H ₂ O ₂ at $-195^{\circ}\text{C}.$	2.79	1.75	1.83	1.22	0.56
H ₂ O at $-195^{\circ}\text{C}.$	5.45	4.82	4.76	4.90	5.41
H ₂ O at $-78^{\circ}\text{C}.$	3.06	3.04	3.44	4.08	4.85

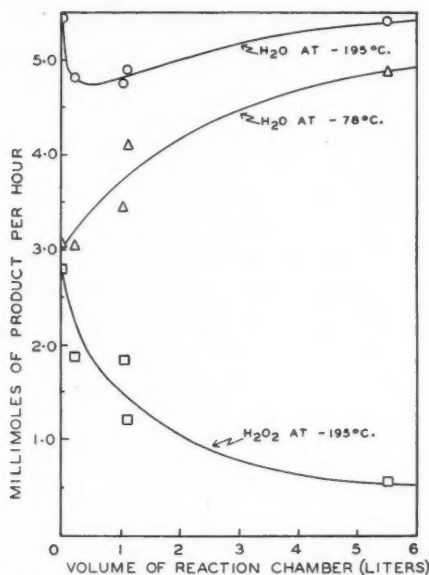


FIG. 5. Influence of reaction chamber volume on water and hydrogen peroxide yields.

obtained, in amounts which increased with increasing chamber volume, and apparently approached an upper limit. At -195°C . both hydrogen peroxide and water were obtained. The yield of water, which was always greater than the corresponding yield at -78°C ., at first decreased with increasing volume and then increased; it must approach the same upper limit as for -78°C . In contrast, the peroxide yield decreased continuously with volume increase, but was still appreciable with the largest chamber.

Influence of Surface

The difference in the results obtained with chambers (2) and (3) (Table II), which were of comparable volume but different in surface-volume ratio, suggested that surface effects were considerable. This was further investigated by loosely filling chamber (2) with 4.3 gm. of Pyrex wool and determining the amounts of water and peroxide obtained at trap temperatures of -78°C . and -195°C . The results are given in Table III, along with data for otherwise identical experiments with the unpacked sphere. At -195°C . the peroxide yield was drastically reduced by packing, but the yield of water was virtually unaltered. At -78°C . more water was obtained with the packed sphere.

In an experiment to determine the effect of surface in the cold trap itself, Pyrex wool was placed along a 5 cm. section of the inlet arm of the trap, just at the level of the cooling bath. The trap was attached directly to the discharge tube and cooled with liquid nitrogen. Table IV gives the results together with comparable data for the unpacked trap. The yield of water was virtually unaffected, but yields of peroxide and evolved oxygen were reduced.

TABLE III
EFFECT OF PACKING REACTION CHAMBER (2)

	Yields: mM. per hour		
	At $-195^{\circ}\text{C}.$		At $-78^{\circ}\text{C}.$
	H_2O_2	H_2O	H_2O
Unpacked	1.83	4.76	3.44
Packed	0.12	4.73	4.54

TABLE IV
EFFECT OF PACKING TRAP

	Yields, at $-195^{\circ}\text{C}.$ mM. per hour				
	H_2O_2	H_2O	Evolved O_2	O_2 gas	H_2 gas
Unpacked	3.74	5.90	0.64	0.31	5.63
Packed	3.62	5.94	0.48	0.56	5.71
Difference	-0.12	+0.04	-0.16	+0.25	+0.08

Discussion

The final products obtained in these experiments were presumably formed by a four-stage process:

(1) Discharge tube stage, in which the water vapor is partially or completely decomposed into H and OH, with possible subsequent interaction of the active species. Apparently, no detectable amounts of hydrogen peroxide issue from the discharge, since none is collected in a following trap at $-78^{\circ}\text{C}.$ However, a certain amount of water does emerge from the discharge. Examination of the curve showing variation of water yield with trap temperature (Fig. 4) shows that with increasing temperature, the yield of water decreases to a lower limit at about $-78^{\circ}\text{C}.$ It may be reasonably assumed that this residual amount of water, which does not vary with trap temperature, is actually the amount entering the trap, and since in this case the trap was attached directly to the discharge tube, is the amount of water emerging from the discharge in all experiments. This is, of course, equivalent to assuming that no appreciable amount of water is formed in the trap at $-78^{\circ}\text{C}.$

(2) Reaction chamber stage, in which reactions involving the active species from the discharge tube proceed at room temperature. Results obtained with reaction chambers of increasing volume (Fig. 5) show that these reactions produce water, hydrogen, and oxygen, since a following trap at $-78^{\circ}\text{C}.$ collects only water in amounts which increase with increasing chamber volume. The actual amount of water formed in a given reaction chamber can be calculated by subtracting the yield at $-78^{\circ}\text{C}.$, with the trap attached directly to the

discharge tube, from the yield at -78°C . with the reaction chamber in question between the discharge and the cold trap. Taking the ultimate yield of water at infinite volume to be 5.5 mM. per hour (Fig. 5), such a calculation shows that 20 weight per cent of the dissociated water vapor leaving the discharge would be converted to water if the reaction were to go to completion at room temperature. Examination of the data for the packed sphere (Table III) reveals that, although in these experiments the reaction had gone almost to completion (shown by the small yield of peroxide and the small increase in yield of water obtained by lowering the trap temperature), only 12 weight per cent of the dissociated water vapor was converted to water. Increasing the surface thus favors the formation of hydrogen and oxygen over the formation of water. Because of this surface effect any quantitative calculation of the rate of disappearance of active species based on the data of Table II would be meaningless. Under some conditions, active species must survive for roughly four seconds, since peroxide was obtained at -195°C . even with the five liter reaction chamber.

(3) Cold trap stage, in which condensable products formed in the reaction chamber or discharge tube are collected, and the active species which have survived passage through the reaction chamber (or have been formed therein), react at a much lower temperature. The nature of the product formed in this stage has not been determined directly, but only by inference from a determination of the products at room temperature.

(4) Warming stage. Above -120°C . the products collected below -150°C . evolve oxygen in amounts proportional to the quantity of product and independent of the temperature of evolution and leave hydrogen peroxide and water in the trap.

By mixing atomic hydrogen and molecular oxygen, Geib and Harteck (6) obtained a product which exhibited the same appearance and behavior as the product found in the present study. Thus, at the temperature of formation, it was glassy and transparent, while at temperatures above -115°C . it gave off oxygen and finally melted to hydrogen peroxide and water. Geib and Harteck suggested that the oxygen was formed by the decomposition of an "abnormal" form of peroxide, $\text{H}_2\text{O} \rightarrow \text{O}$.

Figs. 6 and 7 show respectively the manner in which oxygen: water, and peroxide: water ratios vary with temperature of formation (trap temperature) for the $\text{H}-\text{O}_2$ system, calculated from the data of Geib and Harteck, and for the dissociated water vapor system (calculated from the data of Table I, excluding the water presumed to have entered the trap as such). Evidently, at a given temperature of formation the products of the two systems have nearly the same composition.*

* The closeness of the correlation is to some extent fortuitous. According to the data of Geib and Harteck the composition of the product from the $\text{H}-\text{O}_2$ reaction is dependent on the relative concentrations of H and O_2 and an increase in the H -atom concentration at a given temperature has the same general effect as increasing the temperature. However, the data for this reaction plotted in Figs. 6 and 7 were obtained with a $\text{H}_2:\text{O}_2$ ratio (1.4) not greatly different from that which would correspond to an equimolar mixture of H and OH (2.0), so that the comparison is by no means without significance.

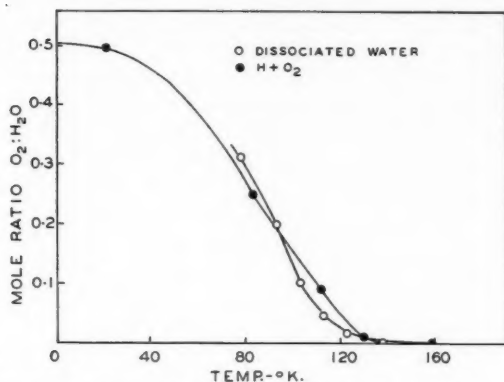


FIG. 6. Oxygen: water ratio at different temperatures for the $H-O_2$ reaction (calculated from data of Geib and Harteck), and for the dissociation of water vapor.

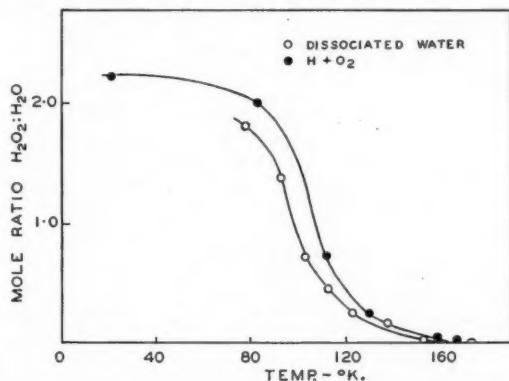


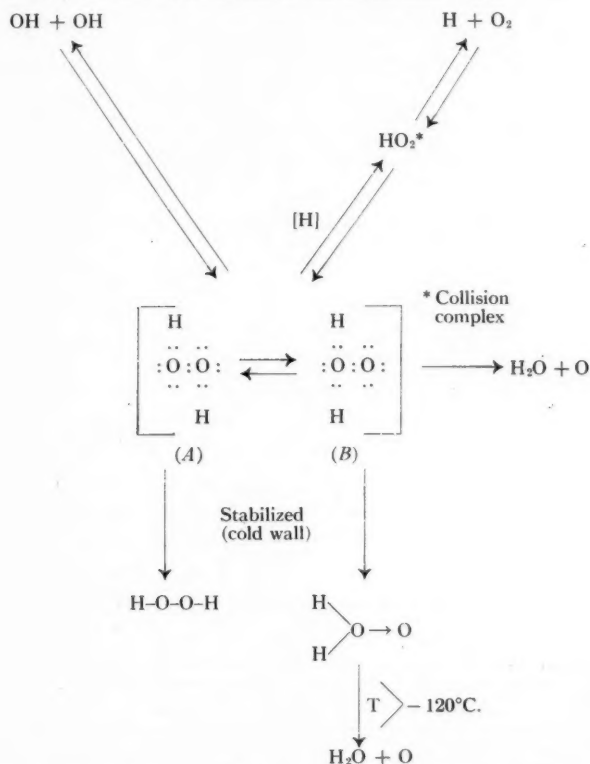
FIG. 7. Hydrogen peroxide: water ratio at different temperatures for the $H-O_2$ reaction (calculated from data of Geib and Harteck), and for the dissociation of water vapor.

The simplest explanation for this correspondence would be that the dissociated water vapor flowing from the discharge tube is actually a mixture of H and O_2 , but the experimental evidence against this is strong (11). Therefore it appears that a mixture of H and OH and appropriate mixtures of H and O_2 yield identical products. This means, presumably, that the same mechanism to form the product operates in the two systems, since it is unlikely that two different mechanisms would show the same temperature dependence.

It is possible to suggest a mechanism which correlates the two systems by adaptation and extension of one already proposed by Badin (1) for the low temperature $H-O_2$ reaction.

It may be represented as shown on the following page. The key unit is an unstable collision complex which exists in two tautomeric (prototropic) forms (*A*) and (*B*) and can be formed by the union of two hydroxyl radicals, or from H and O_2 with the intermediate formation of excited HO_2 . Since the reactions

forming this complex are highly exothermic, it has a high energy content and unless it is stabilized it decomposes soon after it is formed. Decomposition may occur in one of three ways: (1) reversibly into two OH radicals, (2) reversibly into 2H and O_2 , (3) irreversibly into H_2O and O^* . Since H atoms are continuously lost by combination to H_2 , the final products, if stabilization does not occur, are H_2 , O_2 , and H_2O , as observed experimentally.



If, however, the collision complex is stabilized, for instance by collision with a sufficiently cold wall, the reaction takes a different course. Stabilization of (A) forms ordinary hydrogen peroxide, whereas stabilization of (B) forms the "abnormal" peroxide suggested by Geib and Harteck, which supposedly decomposes above -115°C. to water and oxygen.

The gas-phase equilibrium between (A) and (B) may be expected to shift with changing temperature. Experimentally, proportionately more oxygen is evolved from products formed at lower temperatures, from which it may be inferred that a decrease in temperature shifts the equilibrium in favor of form (B).

* It has been reported by Rodebush and Wahl (15) and confirmed by the authors, that oxygen atoms do not react with water at liquid oxygen temperatures.

Probably the major part of the water formed in the cold trap results from the reaction $H + OH + M \rightarrow H_2O + M$, where M is, in most cases, the cold wall. Column 7, Table I, gives the yields for this reaction, calculated on the basis of the proposed mechanism, i.e. assuming that part of the water is formed by the decomposition of peroxide. With decreasing temperature the yield increases to a maximum at -160°C . and then decreases rapidly again. The initial increase is to be expected because of the increasing efficiency of the reaction as the temperature is lowered. The subsequent decrease may be due to the decrease in concentration of OH that results from increased stabilization of $(HO)_2$ complexes.

Badin (1) has already pointed out that a similar intermediate complex has been postulated by Egerton and Minkoff (5) for the reactions at higher pressures between hydrogen and oxygen. Also, Oldenberg and Rieke, in a study (13) of the kinetics of disappearance of OH in the water vapor discharge, conclude that "OH radicals form collision complexes which have a lifetime much greater than the duration of the bimolecular collision between them".

If the suggested mechanism is valid, the interesting conclusion follows that appropriate mixtures of H and OH, on one hand, and H and O_2 on the other, attain to the same chemical composition, virtually instantaneously, and therefore should exhibit identical chemical behavior. Jackson (7) has, in fact, found that a characteristic action of dissociated water vapor, the oxidation of CO to CO_2 , is also displayed by a mixture of H and O_2 .

Acknowledgment

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THE REACTION OF NITROGEN ATOMS WITH METHANE AND ETHANE¹

BY H. BLADES AND C. A. WINKLER

Abstract

Methane reacted with nitrogen atoms at temperatures above 300°C. to produce hydrogen cyanide. An activation energy of 11 kcal. and a steric factor of 5×10^{-3} were obtained. The reaction of ethane with nitrogen atoms was studied up to 295°C., with hydrogen cyanide the only product found in measurable amounts. At high temperatures, nitrogen atom consumption was complete in excess ethane, and the hydrogen cyanide production under these conditions, compared with the atom concentration determined by a Wrede gauge, indicated the active species in the nitrogen stream to be only atomic nitrogen. The ethane-nitrogen atom reaction was second order, with an activation energy of 7 ± 1 kcal. and a steric factor between 10^{-1} and 10^{-3} .

The reaction of nitrogen atoms with ethylene has been discussed in previous papers from this laboratory (1, 2). Similar studies have now been made, using methane and ethane, with the results outlined below.

Experimental

The apparatus was similar in all essential respects to that described in the earlier papers, but certain significant changes in procedure were adopted. Commercial nitrogen was passed over copper turnings at about 500°C. to remove oxygen and was metered into the discharge tube after it had passed through a liquid air trap. Hence, unlike the previous study, the present investigation was made with nitrogen containing no water vapor to act as a wall poison in the reaction vessel and trap immediately following it. These were therefore poisoned with phosphoric acid in the conventional way. With one Wrede gauge at the inlet to the reaction vessel and another at the outlet, the effect of temperature on the concentration of nitrogen atoms during their passage through the reaction chamber was determined. At room temperature the atom concentration decreased by about 50% between the inlet and outlet of the chamber but no decrease was detectable at temperatures of 256°C. and 415°C.

Methane (Matheson Co. Inc.) 99% purity, was used as received. Ethane (Phillips Petroleum, 95% pure) was purified by the method described by MacGillvray (3).

Careful manipulation of the reaction products in the absence of moisture prevented, almost entirely, formation of the hydrogen cyanide polymer that was so troublesome in the earlier study with ethylene. The liquid nitrogen trap immediately following the reaction vessel was allowed to warm to room temperature to transfer the condensed hydrocarbons and hydrogen cyanide to a

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small liquid nitrogen trap that could be later weighed. If, during this operation, the hydrogen cyanide was not allowed to melt, it could be transferred by sublimation with little or no loss by polymerization.

The contents of the small trap were fractionated by raising the temperature to -116°C . (frozen ether slurry) and trapping the distillate in another liquid nitrogen trap. The weight of the residue left at -116°C . was determined, after which 5% potassium hydroxide solution was added and the cyanide content determined volumetrically (4). The quantity of distillate was obtained by expanding it into a standard volume and measuring the pressure. This was followed, when desired, with analysis in a Podbielniak still.

Results

Reaction with Methane

The experimental conditions used, and results obtained; in the study with methane are shown in Table I. In these experiments a small quantity of hydrocarbon (identified by combustion) was obtained from the fractionation at -116°C . Calculated as ethane, it represented about 2% of the methane that had reacted. No consideration has been given to it in setting up Table I.

TABLE I
EXPERIMENTAL AND CALCULATED DATA ON THE
METHANE - ATOMIC NITROGEN REACTION

Total pressure, mm. Hg	Ratio of methane to atomic nitrogen	Temp., $^{\circ}\text{C}$.	Flow rate of atomic nitrogen, moles/min.	Flow rate of methane, moles/min.	Rate of HCN production, moles/min.	Collision yield
1.65	0.282	416	9.23×10^{-4}	2.60×10^{-4}	0.43×10^{-4}	1.79×10^{-6}
1.65	0.675	322	"	6.23	0.44	4.71×10^{-7}
1.65	0.668	370	"	6.14	1.13	1.37×10^{-6}
1.68	0.682	397	"	6.30	2.15	2.74×10^{-6}
1.68	0.688	402	"	6.35	1.10	1.37×10^{-6}
1.76	1.00	425	"	9.26	2.14	1.88×10^{-6}
1.68	1.05	344	6.45×10^{-4}	6.77	0.54	7.66×10^{-7}
1.68	1.08	376	"	6.95	0.75	1.13×10^{-6}
1.71	1.08	389	"	6.98	0.74	1.15×10^{-6}
1.70	1.04	401	"	6.70	1.42	2.62×10^{-6}
1.68	1.08	435	"	6.95	1.21	2.24×10^{-6}
1.93	2.17	377	9.23×10^{-4}	20.1	3.22	1.25×10^{-6}
1.93	"	424	"	19.9	5.71	2.46×10^{-6}
1.93	"	446	"	20.0	5.28	2.38×10^{-6}

Collision yields were calculated in the usual way, using values of 3.75 Å. and 3.0 Å. for the collision diameters of methane and atomic nitrogen respectively.

A plot of \log (collision yield) against $\frac{1}{T}$ (Fig. 1) shows that, with the exception of three points, a reasonably good linear relation is obtained. Since there is no definite trend of collision yield with methane - nitrogen atom ratio, the scatter of points is presumably due only to experimental uncertainties.

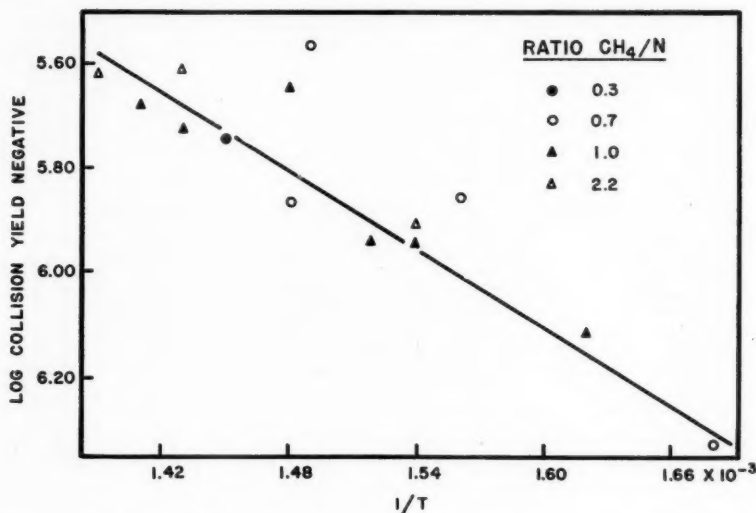


TABLE II

REACTION BETWEEN ETHANE AND NITROGEN ATOMS,
WITH ETHANE IN EXCESS

Temp., °C.	Nitrogen atom* conc., % (Wrede gauge)	Av. mole ratio, ethane atomic nitrogen	Flow rate of ethane, mole/min.	Rate of HCN production, moles/min.	Nitrogen atom conc., % (HCN prod.)
176	12 ± 2	2.7	1.71 × 10 ⁻³	6.9 × 10 ⁻⁴	10 ± 0.3
194	"	"	1.73	6.4	"
208	"	"	1.74	6.6	"
285	"	"	1.72	6.4	"
260	14 ± 1.5	3.4	1.72	5.1	14 ± 0.3
250	9 ± 1.5	2.0	1.70	9.6	7.7 ± 0.3
285	"	"	1.77	8.9	"

* Each value is the mean of six consecutive gauge readings and the uncertainty given is the average deviation of these readings.

In Table III are recorded further data for the reaction, obtained under conditions of temperature and reactant concentrations such that "clean-up" of nitrogen atoms did not occur.

TABLE III

RATE OF PRODUCTION OF HYDROGEN CYANIDE FROM THE ETHANE -
NITROGEN ATOM REACTION UNDER VARIOUS REACTION CONDITIONS

Pres- sure, mm. Hg	Ratio ethane to atomic nitrogen	Temp., °C.	Flow rate of atomic nitrogen, moles/min.	Flow rate of ethane, moles/min.	Rate of HCN production, moles/min.	k_2 calculated by Equation (1)	k_2 calculated by Equation (2)
1.52	0.256	127	9.23 × 10 ⁻⁴	2.36 × 10 ⁻⁴	1.36 × 10 ⁻⁴	3.09 × 10 ⁵	7.86 × 10 ⁵
1.62	0.256	202	9.23	2.36	2.45	8.85	30.1
1.55	0.264	230	9.23	2.44	2.96	14.5	57.0
1.55	0.262	243	9.23	2.42	2.85	14.4	54.6
1.35	0.492	106	9.23	4.54	1.65	2.48	5.31
1.35	0.549	168	9.23	5.06	3.64	8.05	24.5
1.27	0.560	243	9.23	5.17	5.98	29.3	148
1.56	0.567	295	9.23	5.24	6.72	32.3	197
1.25	0.995	109	5.11	5.09	0.975	2.27	5.33
1.35	1.01	192	5.11	5.14	2.36	9.00	28.0
1.26	0.985	264	5.11	5.04	3.32	26.2	110

The rate constant for each experiment was calculated using a second order rate expression,

$$\frac{dx}{dt} = k_2 (a - x) \left(b - \frac{x}{2} \right).$$

where a = partial pressure of atomic nitrogen,
 b = partial pressure of ethane,
 x = partial pressure of hydrogen cyanide.

For no interdiffusion of reaction zones in the reaction vessel, such that the concentrations of reactants change uniformly from the initial values on mixing to the final values determined by the amount of reaction during the flow time, the integrated form is

$$k_2 = \frac{1}{t} \frac{1}{(a - 2b)} \ln \frac{b(a - x)}{a\left(b - \frac{x}{2}\right)} \quad (1)$$

If, however, turbulence is assumed such that the concentrations are uniform throughout the chamber and remain constant at values equal to those found in the gas leaving the reaction vessel, the integrated form is

$$k_2 = \frac{1}{t} \frac{x}{(a - x)\left(b - \frac{x}{2}\right)} \quad (2)$$

Calculations were made using both equations, to obtain the values of k_2 given in Table III. A reasonably satisfactory plot of $\log k_2$ against $\frac{1}{T}$ is obtained using either set of k_2 values (e.g. Fig. 2) but the data are not sufficiently accurate to distinguish the superiority of one treatment over the other. There is little doubt, however, that the reaction is second order.

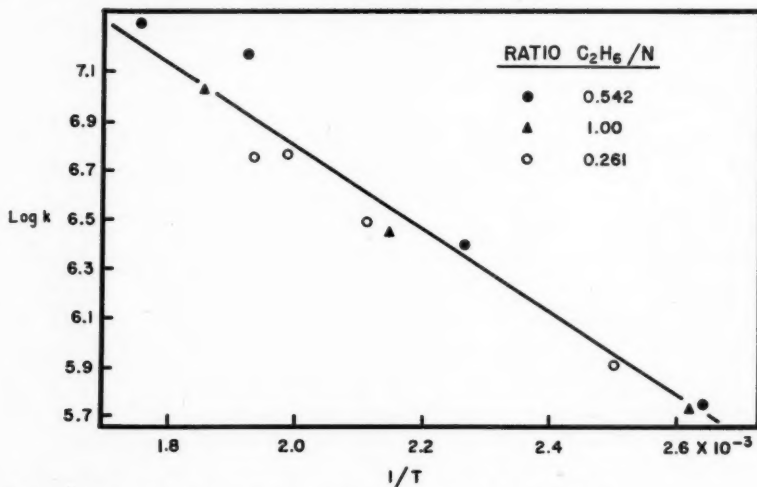


FIG. 2. Plot of $\log k$ versus $1/T$ for the nitrogen atom-ethane reaction.

Activation energy values of 6.2 and 7.9 kcal. were obtained from the Arrhenius lines plotted from the k_2 values given by Equations 1 and 2 respectively. These values may be taken to represent the limits within which the true activation energy probably lies.

The steric factor in the expression $k = PZe^{-E/RT}$ was calculated for values of k at 450°K., taken from the $\log k - \frac{1}{T}$ plots corresponding to Equations (1)

and (2). The value of Z was calculated assuming collision diameters of 3.75\AA . and 3.0\AA . for ethane and atomic nitrogen respectively. For the plot of $\log k$ vs. $\frac{1}{T}$ based on Equation (1), where $E = 6.2$ kcal., $k = 8.1 \times 10^{-6}$ liter mole $^{-1}$ sec. $^{-1}$, and $P = 3 \times 10^{-3}$, while from the corresponding plot based on Equation (2), where $E = 7.9$ kcal., the values were $k = 26.9 \times 10^{-6}$ liter mole $^{-1}$ sec. $^{-1}$ and $P = 7 \times 10^{-2}$.

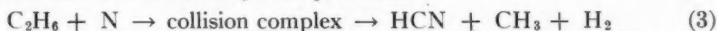
Discussion

Since hydrogen cyanide was the only product obtained from either of the reactions studied, it may be inferred that no nitrogen-containing intermediate of appreciable stability (e.g. ethylenimine) was formed. It also seems unlikely that radicals such as $=\text{NH}$ were present in significant concentration since these might be expected to give rise to ammonia or other nitrogenous products in measurable amounts.

In the present state of inadequate knowledge concerning nitrogen atom reactions generally, there would seem to be no obvious alternative to assuming a mechanism for the present reactions somewhat similar to that suggested previously for the reaction of nitrogen atoms with ethylene (1). With methane, this would be merely



With ethane, the reaction may be represented



It may be assumed that the measured activation energy of 7 ± 1 kcal. for the reaction with ethane is associated with one of the steps prior to Reaction (4), and that Reaction (4) is relatively much faster, to avoid the possibility of methane formation by



While the schemes suggested above have obvious objections, no satisfactory alternatives have yet been devised. Studies, now in progress, of the reactions of atomic nitrogen with propane, propylene, and butane give promise of better understanding of this type of reaction.

Acknowledgment

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SYNTHESIS OF 5-SUBSTITUTED 1-ANILINO-4-IMINOBARBITURIC ACIDS¹

BY PAUL E. GAGNON, JEAN L. BOIVIN,² AND JACQUES GIGUERE³

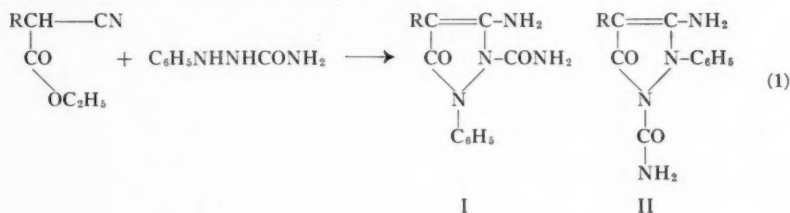
Abstract

Substituted cyanoacetic esters have been reacted with 1-phenylsemicarbazide to give rise to 5-substituted-1-anilino-4-iminobarbituric acids. The presence of an imino substituent in position 4 has been established by the hydrolysis of 5-benzyl-1-anilino-4-iminobarbituric acid into 5-benzyl-1-anilinobarbituric acid. The position of the anilino group has been ascertained by the transformation of 5-octyl-1-anilino-4-iminobarbituric acid into octylcyanoacetic phenylhydrazide, carbon dioxide, and ammonia.

Introduction

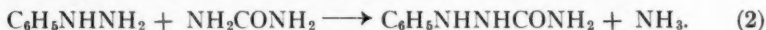
The present investigations were undertaken to study the behavior of 1-phenylsemicarbazide ($C_6H_5NHNHCONH_2$) toward substituted cyanoacetic esters in view of preparing pyrazolones or barbituric acids.

It is known that hydrazine and N-alkyl or N-arylhydrazines react with substituted cyanoacetic esters in the presence of sodium ethylate to give rise to pyrazolones (4, 5, 6, 9). However, 1-phenylsemicarbazide, a derivative of hydrazine, did not yield the expected pyrazolones (I or II) when it was reacted with these esters under the same conditions.



The compounds obtained, like pyrazolones, were soluble in alkaline solution but were insoluble in active acids. The ultraviolet absorption spectra obtained were very different from the spectra of pyrazolones. They were similar in acid and neutral solutions (Table I), whereas the pyrazolones gave different spectra.

It should be noted that 1-phenylsemicarbazide is a derivative of urea and hydrazine which is made by treating urea with phenylhydrazine:



Therefore the reaction products obtained from Equation 1 may be barbituric acids. It is known that urea and substituted ureas like phenylurea react with

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TABLE I
 5-MONOSUBSTITUTED-1-ANILINO-4-IMINOBARBITURIC ACIDS

Substituent	Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
			Nitrogen, %		Neutral		Acid	
			Calc.	Found	Log E_m	$\bar{\Lambda}$	Log E_m	$\bar{\Lambda}$
Methyl	$C_{11}H_{12}O_2N_4$	254-256	24.1	23.9	4.15	2250	4.12	2260
Ethyl	$C_{12}H_{14}O_2N_4$	239-241	22.7	22.4	4.37	2750	4.34	2750
<i>n</i> -Propyl ¹	$C_{13}H_{16}O_2N_4$	222-223	21.5	21.7	4.12	2270	4.12	2260
<i>n</i> -Butyl*	$C_{14}H_{18}O_2N_4$	229-230	20.4	20.6	4.34	2750	4.33	2750
<i>n</i> -Pentyl	$C_{15}H_{20}O_2N_4$	189-191	19.5	19.3	4.29	2750		
<i>n</i> -Hexyl	$C_{16}H_{22}O_2N_4$	122-123	18.5	18.5	4.15	2270	4.22	2270
<i>n</i> -Heptyl ²	$C_{17}H_{24}O_2N_4$	129-130	17.7	17.7	4.36	2740	4.37	2750
<i>n</i> -Octyl	$C_{18}H_{26}O_2N_4$	140-142	16.9	16.7	4.08	2270	4.12	2270
<i>n</i> -Nonyl	$C_{19}H_{28}O_2N_4$	139-141	16.3	16.2	4.26	2740	4.28	2740
<i>n</i> -Decyl	$C_{20}H_{30}O_2N_4$	136-137	15.6	15.9	4.07	2270	4.19	2270
Benzyl	$C_{17}H_{16}O_2N_4$	144-145	18.3	18.5	4.28	2740	4.23	2750
<i>o</i> -Chlorobenzyl	$C_{17}H_{15}O_2ClN_4$	202-203	16.4	16.3	4.14	2270	4.04	2270
β - <i>p</i> -Methylphenoxyethyl ³	$C_{20}H_{19}O_3N_4$	196-197	15.9	15.6	4.27	2740	4.30	2750
γ - <i>p</i> -Methylphenoxypropyl ⁴	$C_{20}H_{22}O_3N_4$	130-131	15.3	15.2	4.05	2270	4.08	2270
β - <i>p</i> -Ethylphenoxyethyl	$C_{20}H_{22}O_3N_4$	197-199	15.3	15.1	4.31	2750	4.26	2750
γ - <i>p</i> -Ethylphenoxypropyl	$C_{21}H_{24}O_3N_4$	128-129	14.7	14.6	4.14	2270	4.12	2250
γ - <i>p</i> -Chlorophenoxypropyl	$C_{19}H_{19}O_3ClN_4$	142-143	14.5	14.5	4.32	2750	4.32	2750
γ - <i>p</i> -Bromophenoxypropyl	$C_{19}H_{19}O_3BrN_4$	126-128	12.9	12.7	4.08	2270	4.04	2270
					4.27	2750	4.29	2760
					4.18	2270	4.05	2270
					4.33	2720	4.29	2750
					4.35	2700	4.37	2700
					4.35	2250	4.34	2270
					4.34	2720	4.29	2740
					4.33	2250	4.32	2250
					4.33	2730	4.31	2750
					4.39	2270	4.45	2270
					4.37	2740	4.36	2740
					4.35	2250	4.32	2270
					4.32	2740	4.31	2740
					4.48	2270	4.38	2270
					4.36	2740	4.32	2740
					4.47	2280	4.47	2270
					4.38	2740	4.38	2740

¹In alkaline solution: log E_m , 4.18 and 4.15 at 2250 and 2750 Å.

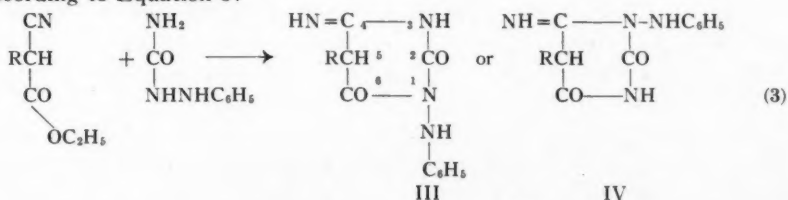
²" " " " " " 4.15 at 2750.

³" " " " " " 4.36 and 4.17 at 2250 and 2740.

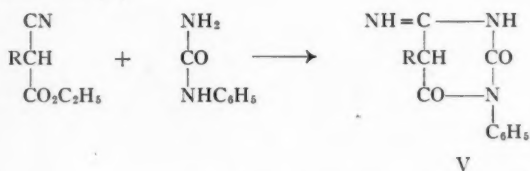
⁴" " " " " " 4.36 and 4.20 at 2230 and 2740.

 *Calc. for $C_{14}H_{18}O_2N_4$: C, 61.3%; H, 6.6%. Found, 61.0%; H, 6.9%.

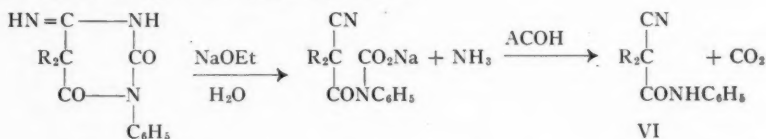
cyanoacetic esters to yield iminobarbituric acids (2, 3, 7, 8). Hence, the following structures (III or IV) may be written for the compounds prepared according to Equation 3:



A survey of the literature revealed that substituted malonic esters condensed with 1-phenylsemicarbazide in the presence of an alkaline catalyst to yield 5-substituted-1-anilinobarbituric acids (1), although no proof of structure was given for these compounds. However, Conrad and Zart (2, 3) prepared many barbituric acids from cyanoacetic esters and phenylurea and gave evidence that formula V represents the correct structure for 5-substituted-1-phenyl-4-iminobarbituric acids (V).

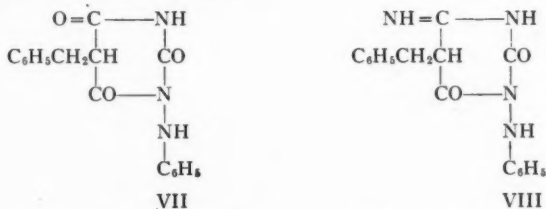


When compound V was reacted with sodium ethylate in sealed tube at high temperature, cyanoacetic anilide (VI), carbon dioxide, and ammonia were formed according to the following scheme:



From the work of Conrad and Zart it is believed that phenylurea and 1-phenylsemicarbazide should react in the same way with substituted cyanoacetic esters, and the formation of pyrazolones should be eliminated.

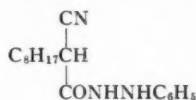
5-Benzyl-1-anilinobarbituric acid (VII) was prepared from benzylmalonic ester and 1-phenylsemicarbazide. By reacting under similar conditions benzylcyanoacetic ester with phenylsemicarbazide, 5-benzyl-4-imino-1- (or -3-) anilinobarbituric acid (VIII) was obtained.



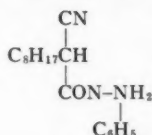
When 5, 5 substituted-1-phenylbarbituric acids were hydrolyzed in alkaline solution, a substance was formed which was identical with 5-benzyl-1-anilinobarbituric acid (VII). This proves that all the compounds prepared have either an actual or potential imino substituent in position 4 which is hydrolyzed into an oxo group.

The anilino substituent may be in position 1 or 3 depending on the reactivity of the cyano group of substituted cyanoacetic esters towards an amido group.

Using the method of Conrad and Zart to open the ring of barbituric acids, 5-octyl-4-imino-1 (or-3-)anilinobarbituric acid was treated with sodium ethylate at 160°C. A compound was obtained which was insoluble in aqueous alkaline solution. Its elemental analysis corresponded to the structures IX and X.

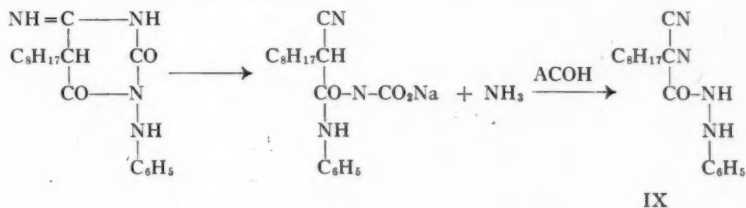


IX



X

Structure X was eliminated because the compound failed to react with aldehydes. Therefore, structure IX should be correct. This indicates that 5-substituted-1-anilino-4-iminobarbituric acids behave the same way as 5, 5-substituted-1-phenylbarbituric acids.



IX

From this study, it is concluded that 1-phenylsemicarbazide is a substance similar to phenylurea and its reaction with substituted cyanoacetic esters gives 5-substituted-1-anilino-4-iminobarbituric acids in good yields.

Experimental

5-Substituted-1-anilino-4-iminobarbituric Acids

To a cold solution of sodium (0.12 mole) in dry ethanol, substituted cyanoacetic ethyl ester (0.06 mole) and 1-phenylsemicarbazide (0.06 mole) were added. The mixture was refluxed in an oil bath at 150°C. for eight hours. The alcohol was evaporated under reduced pressure, and boiling water (250 ml.) was added to the residue. The solution was cooled and extracted with ether to remove unchanged reactants. The aqueous layer was treated with acetic acid until precipitation was complete. The solid was filtered, washed with water, and crystallized from dilute acetic acid.

The white crystalline barbituric acids were obtained in 75 to 85% yields. They are listed in Table I together with their analyses, melting points, and spectrophotometric data. Fig. 1 shows the curves obtained with 5-heptyl-4-imino-1-anilinobarbituric acid. The experimental details for the spectra measurements of similar compounds have been given previously (5).

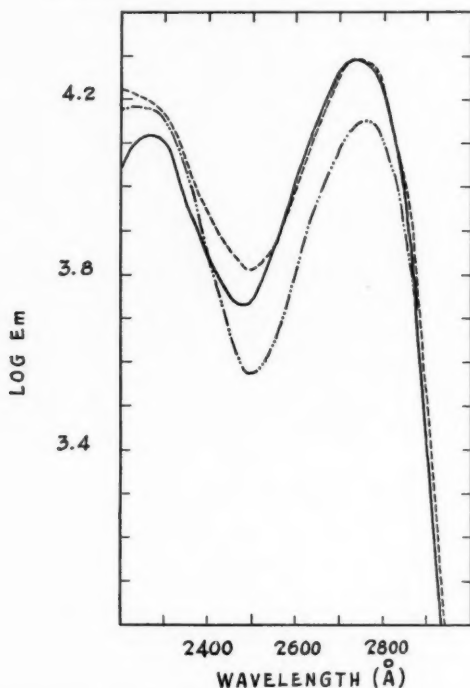


FIG. 1. Ultraviolet absorption spectra.

- 5-Heptyl-4-imino-1-anilinobarbituric acid (95% ethanol).
- - - 5-Heptyl-4-imino-1-anilinobarbituric acid (0.01 N hydrochloric acid in ethanol).
- · - · 5-Heptyl-4-imino-1-anilinobarbituric acid (0.01 N sodium hydroxide in ethanol).

5-Benzyl-1-anilinobarbituric Acid

To a solution of sodium (2.8 gm., 0.06 mole) in absolute ethanol (80 ml.) were added diethyl benzylmalonate (15 gm., 0.06 mole) and 1-phenylsemicarbazide (9.0 gm., 0.06 mole). The reaction mixture was refluxed for six hours at 150°C. The alcohol was evaporated and the residue dissolved in water. The solution was extracted with ether and the aqueous layer treated with hydrochloric acid until a pH of 2 was reached. A precipitate was formed which was crystallized from dilute ethanol: m.p. 107°C. Calc. for $C_{17}H_{16}O_3N_3$: N, 13.6%. Found: N, 13.9%.

5-Benzyl-1-anilino-4-iminobarbituric acid (2 gm.) was dissolved in an aqueous solution of sodium hydroxide (5%, 100 ml.). The solution was refluxed overnight while ammonia was evolved. The solution was treated with acetic acid until precipitation was complete. This precipitate was filtered off and discarded; it was the starting material. By adding hydrochloric acid until a pH of 2 was reached a new compound precipitated out which was crystallized

from dilute ethanol: m.p. 107°C. A mixed melting point determination showed that the substance was identical with 5-benzyl-1-anilinobarbituric acid.

Hydrolysis of 5-octyl-1-anilino-4-iminobarbituric Acid

5-Octyl-1-anilino-4-iminobarbituric acid (0.33 gm., 0.001 mole) was dissolved in a solution of sodium (0.023 gm., 0.001 mole) in absolute ethanol (5 ml.). The solution was heated in a sealed tube at 165-170°C. for two hours. When the tube was opened, ammonia was evolved and a white solid was present in the mixture. Water (25 ml.) was added to dissolve the white solid. The solution was neutralized with acetic acid. Carbon dioxide was evolved and a substance precipitated. The mixture was extracted with ether. The aqueous layer did not contain any phenylhydrazine; a derivative could not be obtained with benzaldehyde. The ethereal solution was washed with sodium carbonate and water, dried over sodium sulphate, and evaporated *in vacuo*. A crystalline compound was obtained: m.p. 121-123°C. A recrystallization from ethanol raised the melting point to 125-126°C.

This compound was insoluble in water and aqueous alkaline solutions. It did not react with benzaldehyde. The substance was octylcyanoacetic phenylhydrazide (IX). Calc. for $C_{17}H_{25}ON$: N, 14.6%. Found: N, 14.8%.

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NOTE

Synthesis of *cis*- and *trans*-1, 2-Dichlorethylene-*d*¹

The infrared absorption spectra of *cis*- and *trans*-dichlorethylene and their completely deuterated analogues were recently reinvestigated by Bernstein and Ramsay (1). In order to complete this work it was felt that *cis*- and *trans*-1, 2-dichlorethylene containing one atom of deuterium should be synthesized.

We had expected to obtain one of the desired compounds, probably *cis*-dichlorethylene-*d*, in two steps by the following reactions: (a) mercuration of *trans*-dichlorethylene with mercuric oxide and a trace of mercuric cyanide in the presence of sodium ethylate to mercury *bis*-dichlorethylenide, $(\text{CHCl}:\text{CCl})_2\text{Hg}$, as described by Fitzgibbon (2); (b) hydrolysis of the mercurial in deuterium oxide containing deuterium chloride. Despite several attempts to mercurate *trans*-dichlorethylene according to the directions given by Fitzgibbon, we were never able to isolate more than traces of the mercurial which he claimed. In our experience mercury *bis*-chloracetylde, $(\text{CCl}:\text{C})_2\text{Hg}$, was always obtained in addition to a large amount of polymercured material.

The literature contains several references to the preparation of haloalkenes from salts of polyhalogenated fatty acids (7). In the present instance, sodium β -deutero- α,β,β -trichloropropionate might be expected to yield *cis*-dichlorethylene-*d*. The ordinary acid, which had not been previously reported, was prepared by chlorinating *trans*- β -chloracrylic acid at 0°C. in carbon disulphide. The *trans*- β -chloracrylic acid was in turn synthesized from propiolic acid as reported by Gryszkiewicz-Trochimowski and Schmidt (3). α,β,β -Trichloropropionic acid crystallizes from petroleum ether in white needles, m.p. 54-55°C. Neutralization equivalent: Calc. for $\text{C}_3\text{H}_3\text{Cl}_3\text{O}_2$: 177.5. Found: 176. The anilide melted at 121-122°C. When sodium α,β,β -trichloropropionate was heated under reflux in aqueous sodium carbonate, only one mole of carbon dioxide was evolved and no dichlorethylene was obtained. Apparently, hydrogen chloride was first eliminated to give a β -dichloracrylic acid which is reported to be stable in aqueous solution. It was isolated from the reaction mixture and identified by its m.p., 85-86°C., as well as that of its amide, 133-134°C. Neutralization equivalent: Calc. for $\text{C}_3\text{H}_2\text{Cl}_2\text{O}_2$: 141. Found: 143. In view of the unexpected course of the reaction, the preparation of the deuterated trichloropropionic acid was not undertaken.

Another possible route to the desired compounds appeared to be the replacement of the carboxyl group in the silver salt of α -deutero- β -bromo- α,β -dichloropropionic acid, $\text{CHBrClCDClCO}_2\text{Ag}$, by heating it under reflux with bromine in carbon tetrachloride to give 1, 2-dibromo-1, 2-dichloroethane-*d*,

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CHBrClCDBrCl. As far as is known, halogenated propionic acids have not been subjected to this reaction (5). In preliminary experiments with the silver salt of the ordinary halogenated propionic acid, the yield of polyhalide was low. For this reason the synthesis of the deuterated acid was abandoned.

It occurred to us at this stage that if deuterium bromide could be made to add abnormally to trichlorethylene, 2-bromo-1,1,2-trichlorethane-1-*d*, $\text{CDCl}_2\text{CHClBr}$, would result. This intermediate, like 1, 2-dichloro-1, 2-dibromoethane-*d* mentioned above, could then be dehalogenated to *cis*- and *trans*-dichlorethylene-*d* with zinc dust in ethanol. The abnormal addition of hydrogen bromide to trichlorethylene has been carried out by Kharasch, Norton, and Mayo (4) in the presence of ultraviolet light and peroxides. In the present work, a sealed tube containing trichlorethylene, deuterium bromide, and dibenzoylperoxide was irradiated for 42 hr. A nearly quantitative yield of 2-bromo-1,1,2-trichlorethane-1-*d*, b.p. 70-72°C. under 22 mm., n_D^{20} : 1.5295, was obtained. By treating the tetrahalide with zinc dust in ethanol, a mixture of *cis*- and *trans*-1, 2-dichlorethylene-*d* was formed. The isomers were separated by careful fractionation in a column packed with glass helices and finally distilled on a vacuum line.

In view of the fact that trichlorethylene undergoes exchange only in the presence of hydroxyl or deuterioyl ions (6), it appeared unlikely that the compounds contained any ordinary dichlorethylene or dichlorethylene- d_2 . Analysis by mass spectrometry did not definitely rule out this possibility but preliminary measurements of the infrared spectrum of each compound did not reveal significant amounts of 1, 2-dichlorethylene or its dideuterated analogue.

The results of a detailed examination of the spectra of these compounds will appear at a later date in a paper by H. J. Bernstein and A. D. Pullin.

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Contents

	Page
The Structure of Ryanodine. I— <i>R. B. Kelly, D. J. Whittingham, and K. Wiesner</i> - - - - -	905
Studies in the Polyoxyphenol Series. V. Preparation from Pyrogallol of the Isomeric Cyclohexane-1,2,3-triols and -1,2-diols, and of Several Isopropylidene and Monomethyl Derivatives— <i>W. R. Christian, C. J. Gogek, and C. B. Purves</i> - - - - -	911
Relative Stabilities of the Isomeric Cyclohexane-1,2,3-triol Trinitrates and 1,2-diol Dintrates— <i>W. R. Christian and C. B. Purves</i> - - - - -	926
An Improved Synthesis of <i>cis-cis-trans</i> -Cyclohexane-1,2,3-triol— <i>C. J. Gogek, R. Y. Moir, J. A. McRae, and C. B. Purves</i> - - - - -	938
The Benzoate and the Methyl Ether of 4-Hydroxycyclohexene— <i>C. J. Gogek, R. Y. Moir, and C. B. Purves</i> - - - - -	946
The Role of Alpha-Ketols in the Low-Sugar Redox Recipe for Low Temperature Emulsion Copolymerization— <i>R. J. Orr and H. Leverne Williams</i> - - - - -	949
The Papilionaceous Alkaloids. XIV. Concerning Spathulatine and Nonalupine— <i>Léo Marion</i> - - - - -	959
The Biogenesis of Alkaloids. III. A Study of Hyoscyamine Biosynthesis Using Isotopic Putrescine— <i>D. G. M. Diaper, Sam Kirkwood, and Léo Marion</i> - - - - -	964
Hydrolysis and Polymerization of Cyclic Dimethylethylene Oxalates— <i>L. G. Ripley and R. W. Watson</i> - - - - -	970
Cupriethylenediamine as a Reagent for Hemicellulose Separation from Wheat Straw Holocellulose— <i>V. D. Harwood</i> - - - - -	974
Influence de Gaz Etrangers sur la Flamme Froide de l'Ether— <i>Ludovic Ouellet and Cyrias Ouellet</i> - - - - -	986
The Rheological Properties of Some Soap-Oil Systems— <i>G. B. Moses and I. E. Puddington</i> - - - - -	996
Reactions in Dissociated Water Vapor— <i>R. A. Jones and C. A. Winkler</i> - - - - -	1010
The Reaction of Nitrogen Atoms with Methane and Ethane— <i>H. Blades and C. A. Winkler</i> - - - - -	1022
Synthesis of 5-Substituted 1-Anilino-4-iminobarbituric Acids— <i>Paul E. Gagnon, Jean L. Boivin, and Jacques Giguere</i> - - - - -	1028
Synthesis of <i>cis</i> - and <i>trans</i> -1,2-Dichlorethylene- <i>d</i> — <i>L. C. Leitch and A. T. Morse</i> - - - - -	1034

